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Operational Characteristics of the Differential Dynamometer: Conductometric Titrations

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OPERATIONAL CHARACTERISTICS OF THE DIFFERENTIAL DYNAMOMETER: CONDUCTOMETRIC TITRATIONS

A Thesis submitted in partial fulfillment of the requirements for the Degree of Master of Science in Loyola University

1939

by

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VITA

The author was born in Chicago, Illinois, in 1914, received his high-school diploma from Loyola Academy in 1932 and his B.S. from Loyola University, Chicago, in 1936. During the school year of 1936-37 he held the position of Graduate Assistant in Chemistry at Loyola University and the following year was a Fellow in Chemistry at the same University.

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I. INTRODUCTION

Among the many properties of solutions of electrolytes the property of conduction of an electric current is of prime importance. During the investigation of this property it was discovered that measurements of conductance follow laws so rigid that this property could be used as a means of quantitative investigation. As a tool for research, for gaining insight into the mechanisms of reactions, conductometric methods are unique. However, the somewhat elaborate set-up has not encouraged the use of this tool commercially.

Recently, in our laboratories, an instrument has been constructed which makes conductometric measurements a simple procedure. The instruments previously used give excellent results. We are then in a position to decide the worth of this instrument by comparing its performance with standard methods. The investigation of the use, properties, and operational characteristics is the purpose for which this included work has been done.

I should like to express my appreciation to Dr. J. D. Parent, under whose inestimable guidance this work was conceived and progressed.

II. THEORY OF CONDUCTOMETRIC ANALYSIS

A.CONDUCTIVITY OF ELECTROLYTES

One of the characteristics of electrolytes is that they conduct an electric current. Because of this property the laws governing conductors of electrocity are applicable to electrolytic conduction in practically the same way as they apply to metallic conductors. Investigation has shown that electrolytic conduction is due to the presence of charged particles called ions.

Ohm's Law states that $E = IR$ where E is the applied electro-motive force, I is the current, and R is the resistance. The usual expression of these units is in volts, amperes, ohms, respectivly. The concept of conductivity is mathematically expressed as the reciprocal of the resistance, or $L' = I/R$ where L' is the conductance expressible in reciprocal ohms (or mhos). Substituting this value in the equation for Ohm's Law, $L'E = I$. [I]

Conductance may also be expressed as specific conductance which is,defined as the conductance of one cubic centimeter of solution. Since conductance is directly proportional to the cross-section (q) of a conductor and inversely as its length (l), we may say that $L' = Lq/l$ where L is the specific conductance.

I. Millard, Physical Chemistry for Colleges, p. I90-I98

Since L may often be uninformative, we may introduce another concept, equivalent conduction (Λ), which is defined as the conduction of a solution containing one chemical equivalent of solute between two electrodes one centimeter apart. A solution of any equivalent concentration C has an equivalent conductance related to the specific conductance by the equation

$$\Lambda = \frac{1000}{C} L$$

A decrease in concentration would results in a decrease of L since fewer ions would be present to conduct the current, but Λ would increase since we do not remove ions but merely increase the distance between them so that inter-ionic attraction falls and therefore mobility increases.

If we decrease the concentration enough we will reach a limiting value of constant equivalent conduction. The solution may then be considered as infinitely diluted and we may then define limiting equivalent conduction as the equivalent conduction of a solution at infinite dilution. This is symbolized by Λ_∞.

Kohlrausch has stated and experimentally verified the law that at infinite dilution the conduction of a solution is equal to the sum of the conductances of the individual ions. This law holds fairly well even for dilute solutions and so we may say that the conductivity of any solution is

some function of the sum of the conductivities of the respective ions.

Experimental evidence indicates that conductivity increases with temperature. The increase is roughly about two percent per degree rise. This is just about the same as the percent decrease in viscosity, and therefore we may assume that conductivity increases with temperature because the viscosity of the solvent is decreased. The kinetic picture is easily verified. At a lower viscosity ions are more free to move and will therefore possess a smaller resistance.

We may then say that the conductivity of any solution depends upon three factors. First, the mobilities of the respective ions. Secondly, the concentration of the ions. Thirdly, the temperature.

B. MEASUREMENT OF CONDUCTION

Conduction is not usually measured directly but rather is calculated from direct resistance measurements. The usual Wheatstone bridge is used (Fig.I). The unknown resistance R_c is compared with three known resistances R_b, ab, and ac. R_b indicates an ordinary resistance box. ab and ac are lengths of unifrm resistance wire. The lengths may be used since resistance is inversely proportional to the length of a conductor. When the E.M.F. at points d and b are equal,

no current passes between these points and any instrument capable of detecting current hooked in between these points will indicate this point of balance. The bridge is balanced by adjusting the three known resistances.

For measuring resistances of metallic conductors direct current is used. If this were attempted with an electrolytic conductor polarization and electrode reactions would occur. Since this would change the effective concentration of the solution, direct current is not permissible. Alternating current is used, of such a frequency that electrode reactions cannot take place and polarization is minimized. Furthermore, even with alternating current, electrode reactions may take place between the metal of the electrodes and the dissolved electrolyte. Therefore an 'unattackable' electrode must be used. Platinum is universally employed for this purpose.

Direct current measurements are easily done because of the simplicity with which the null-point may be detected with a galvanometer. Since we are using alternating current a galvanometer cannot be used. The usual substitute is a telephone (T, Fig.I). The bridge is considered balanced when there is a minimum of sound from the 'phone.

This is the funtamental set-up for most conductivity apparatus. All 'special methods, as reviewed by Britton[2]

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2. Britton, Conductometric Analysis, Chapt. IV

are devices for locating the null-point more easily and accurately. Crystal and therm-ionic valves have been used, along with thermo-crosses and A.C. milliammeters. In all cases, the bridge is balanced and the unknown resistance related to the known resistances by $R_b : R_c :: ab : ac$.

III. APPARATUS

A. THE DIFFERENTIAL DYNAMOMETER

The differential dynamometer is an instrument for measuring resistance directly from scale readings in ohms or some simple multiple of ohms. The readings are continuous and thus there is no need of balancing a bridge. The fundamental diagram is shown in Fig. 2 .

F, F are equal fields from coils connected directly across a 60 cycle, II0 volt A.C. line. C_2 and C_3 are crossed coils wound in such a way that their fields are opposite in polarity to the closest F field. Since the current is alternating, any reversals in polarity of one field is accompanied by equal and opposite reversals of polarity in the other three fields. One arm of each crossed-coil is fed by a line across the A.C. source and is protected by a resistance R_I. Feeding into the second arm of each crossed-coil is current from the second source-line, but each of these feed-lines passes through a resistance of its own, R_2 and R_3 respectively. Assuming equal resistance in the crossed-coils, C_2 and C_3 will have the same field intensity when R_2 and R_3 are equal. Under this condition there will be an equal and opposite torque produced on the indicator needle and it will rest in the middle as shown on the figure. Suppose that we change one of these resistances

R_2 for example. Then the field intensity of C_2 will be changed and the torque balance changed. The needle will then swing in such a way as to equalize the torques. Thus the deflection of the needle will be a function of the change of resistance in R_2 when R_3 is constant.

If we replace R_2 by a conductivity cell, then the deflection of the needle registers its resistance. The scale may, of course, be calibrated in ohms. By making R_3 a known variable, the range of R_2 is amplified. By inserting a variable resistance across R_3 line the needle can always be adjusted to a zero-reading. These and other enlargements of the desing have gone into the construction of the dynamometer as it was used for this work. For a complete discussion of the construction, calibration, and theory of the differential dynamometer, the original paper should be consulted.[3]

B. ACCESSORY APPARATUS

The titrations were carried out in a liter beaker containing approximately 600 cc. of distilled water at room temperature. A motor-driven stirrer was used. The reagents were added from an ordinary 50 ml. buret.

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3. C. A. Crowley, A Study of Conductivity Methods Research paper, Loyola University, Chicago, Illinois

The platinum electrodes (Fig. 3), connected to the dynamometer by means of mercury contacts, were of special design. The main feature of the electrodes is the adjustable distance between the two.
The platinum was kept bright for all determinations, contrary to the usual procedure of blackening them by means of electro-deposited platinum black.

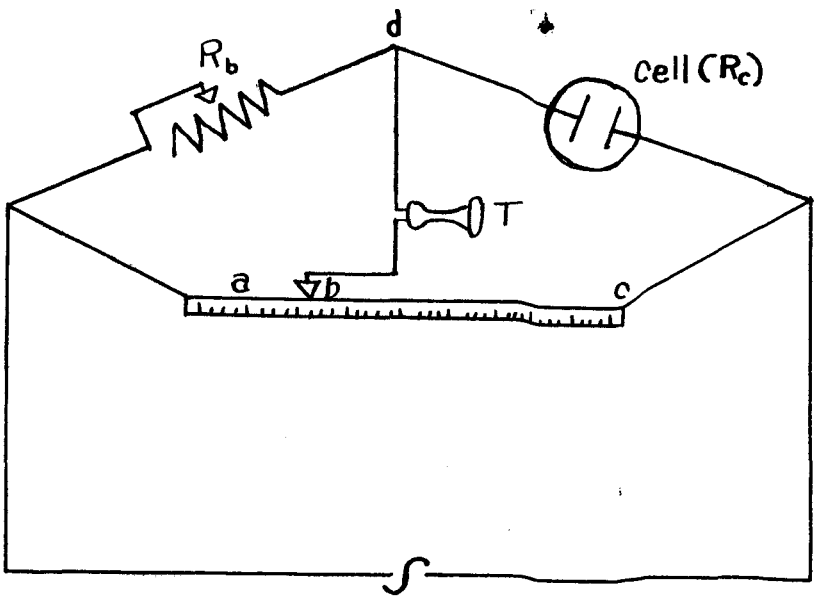

FIGURE I[I]

Arrangement of Wheatstone Bridge for conductivity measurements.

I. Millard, Op. Cit. p.I96

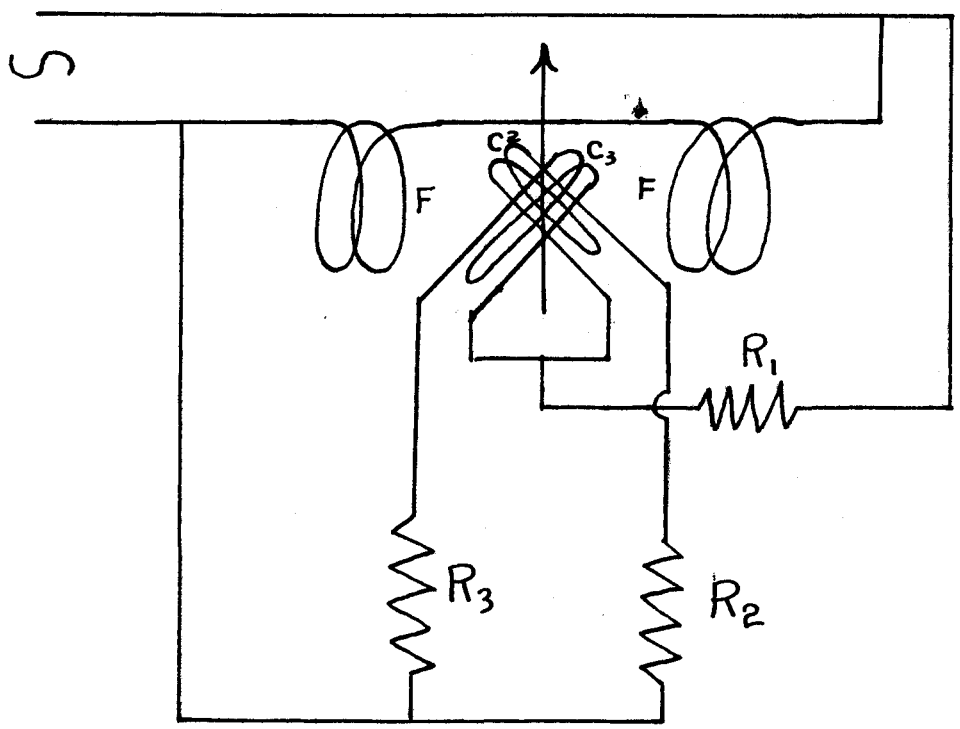

FIGURE 2

Essential diagram of dynamometer hook-up

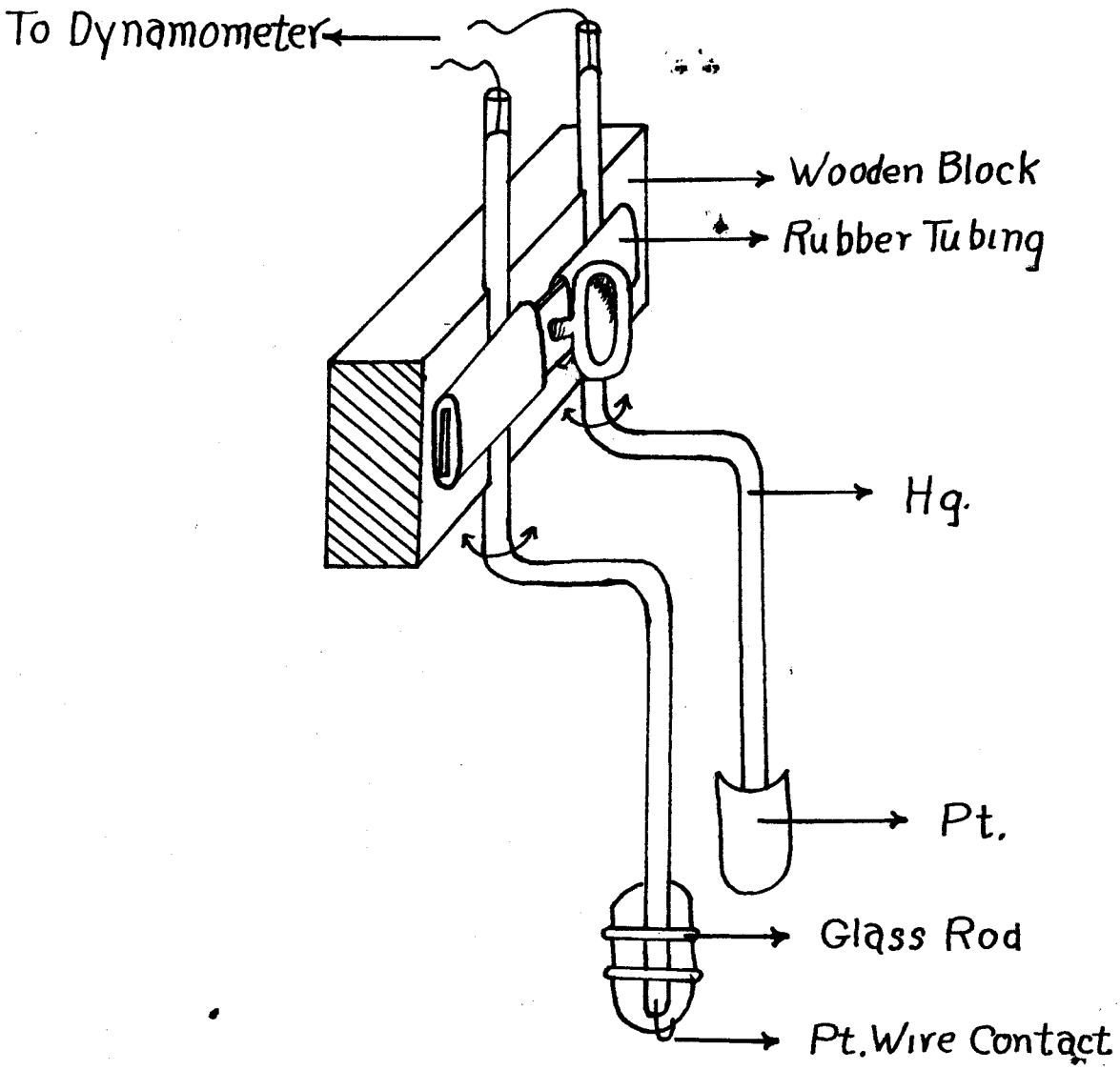

FIGURE 3

Construction of the electrodes used

IV. GENERAL CONSIDERATIONS

A. READINGS OF THE DYNAMOMETER

The dynamometer reads ohmic resistance from 0 to 800. The scale is applicable over three ranges, I/5 X , X , and I2.5 X , where X is the scale reading. These ranges, in conjunction with the variable electrodes, make the dynamometer applicable to all ordinary conductometric titrations. The instrument has been calibrated against known resistances and calibration curves drawn.[4] However, it has been noticed that the scale reading is practically a linear function of the resistance for a greater part of the scale. There is therefore an optimum part of the scale within which one need not correct for by means of the calibration curves (Fig.4). There is no need to know actual resistance if successive readings are linearly related. Furthermore, one need not plot reciprocal scale readings as such, but may plot some simple multiple of I/R, such as IO/R, IOO/R, etc. In the following work conductance is taken as IOOO/R merely for ease of plotting. This sustially gives two figures to the left of the decimal.

B. STIRRING

Continuous stirring was employed. The reading for a given solution varies slightly when the solution is

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4. See footnote, p. 8

stirred and when it is not stirred.

C. TEMPERATURE EFFECTS

Temperature effects were neglected since a thermostat would not be conducive to simplicity. The temperature rise in an ordinary titration is negligible.[5] Even if the temperature rise were appreciable, the end point would be unaffected (Fig.5).

D. CONSTANCY OF ELECTRODE POSITION

The electrodes must maintain the same relative position in the beaker through-out the run, since it was noticed that the reading varies for a given solution depending upon whether the electrodes are near the wall of the container or near the middle. The complete explaination of this phenominon is being investigated, but for our purposes it is sufficient to stree the need of immobilizing the elctrodes once a titration has begun.

E. CONSTANCY OF READINGS

The dynamometer does not give constant readings unless it has been turned on for about fifteen minutes. This is due to the heat effcts on the various resistances and until an equilibrium is established, the instrument should not be used.

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5. Kolthoff and Sandell, Textbook of Quantitative Inorganic Analysis, p. 489

F. THE TIME FACTOR

After the addition of a reagent, the indicator needle will change if there has been a change in resistance. But in some cases, as in the volumetric sulphate determination (vide infra), the initial change does not indicate equilibrium conditions. The needle will change its position withtime. Therefore one must check two consequtive and equal readings over about a half-minute period. Furthermore the torque produced by a change in resistance may be less than that necessary to overcome the friction of the moving coil, and therefore the dynamometer must be tapped in order to allow the needle to come to rest. In general, these precautions are not necessary, but proper technique includes them as a part of the procedure.

G. ADJUSTING THE ELECTRODES

Once a suitable range has been chosen for a given electrolyte in the titration cell, the needle may be brought over any desired part of the scale by adjusting the distance between the electrodes. The value of this is obvious. If the resistance is to increase and then decrease, as in the case of a strong acid - strong base titration, the needle may be brought over the left-hand section of the scale and therefore be kept on the optimum section through

out the entire titration. This can easily be predetermined by a consideration of ionic exchange, as will be brought out later.

H. PLOTTING AND INTERPRETATION OF DATA

The plotting of data and the interpretation of the curve are largely a matter of judgement and control titrations. It is not always advisable to adhere to the general rule that data should be plotted only as accurately as the least accurate experimental value. For example, suppose that a system gave two lines, one of which is parallel to the abscissa and the other has a slight positive slope. Obviously the intersection cannot be determined with a high degree of accuracy. If, however, we increase the modulus of the ordinate, the slope of the second line will be increased and the intersection more clearly defined. Since too great an increase in the modulus of the ordinate will spread the points apart, it is clear that no definite rule can be laid down.

I. PREDETERMINING THE CURVE

It is not always possible to predetermine exactly how the curve should be drawn. One may not always extrapolate past the points near the end point. The only solution is to run control titrations, and from calculated end points determine the drawing. Examples are shown later.

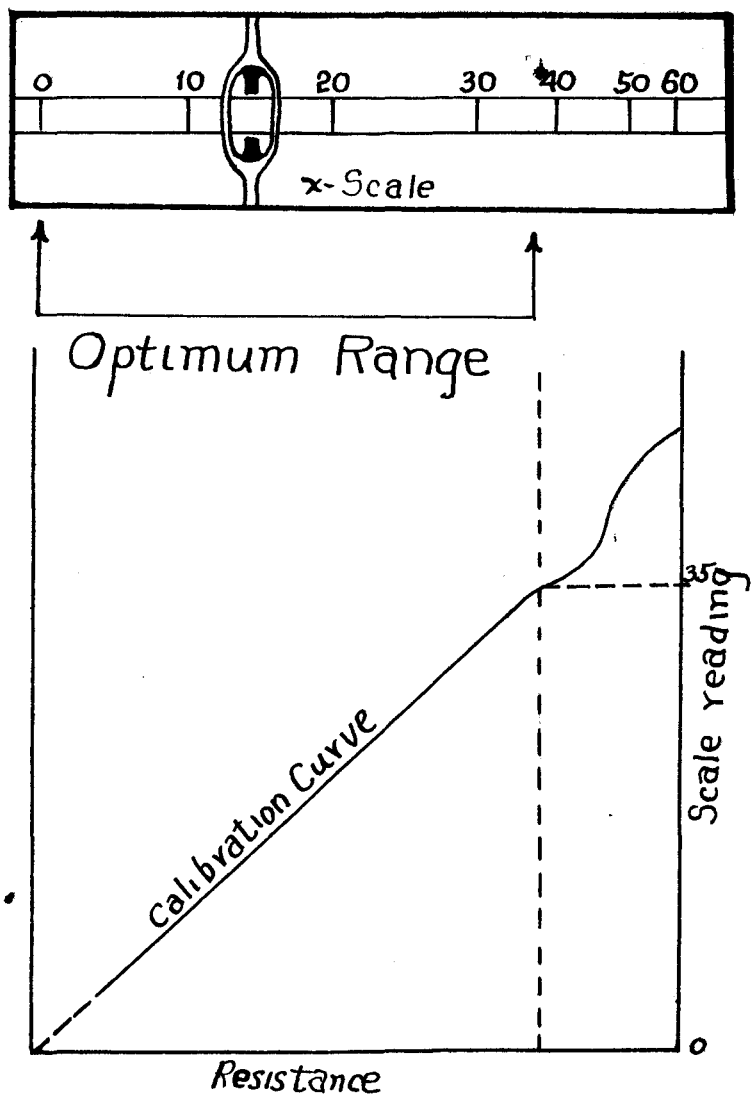


FIGURE 4

Optimum range of dynamometer scale

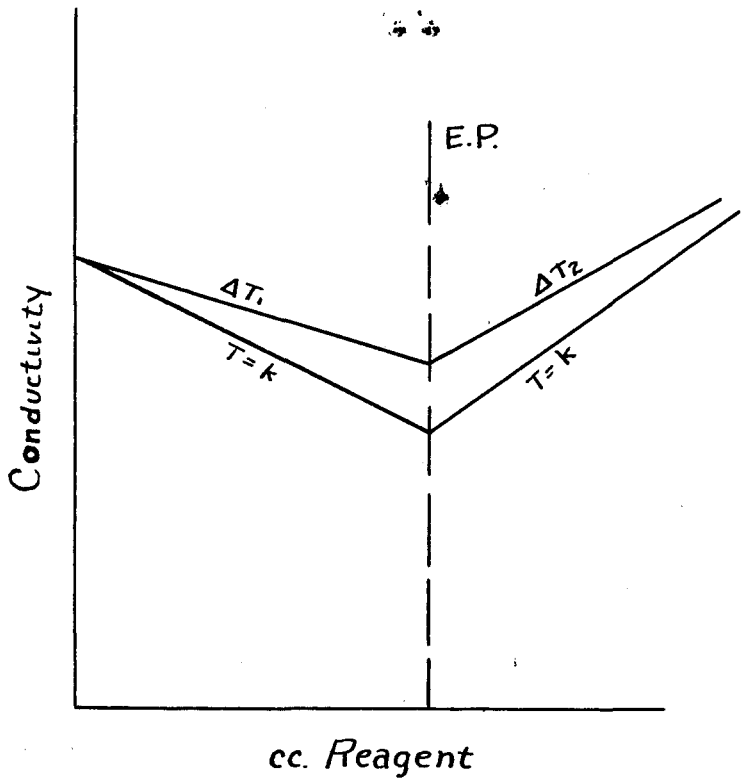


FIGURE 5

Effect of temperature on conductometric titration

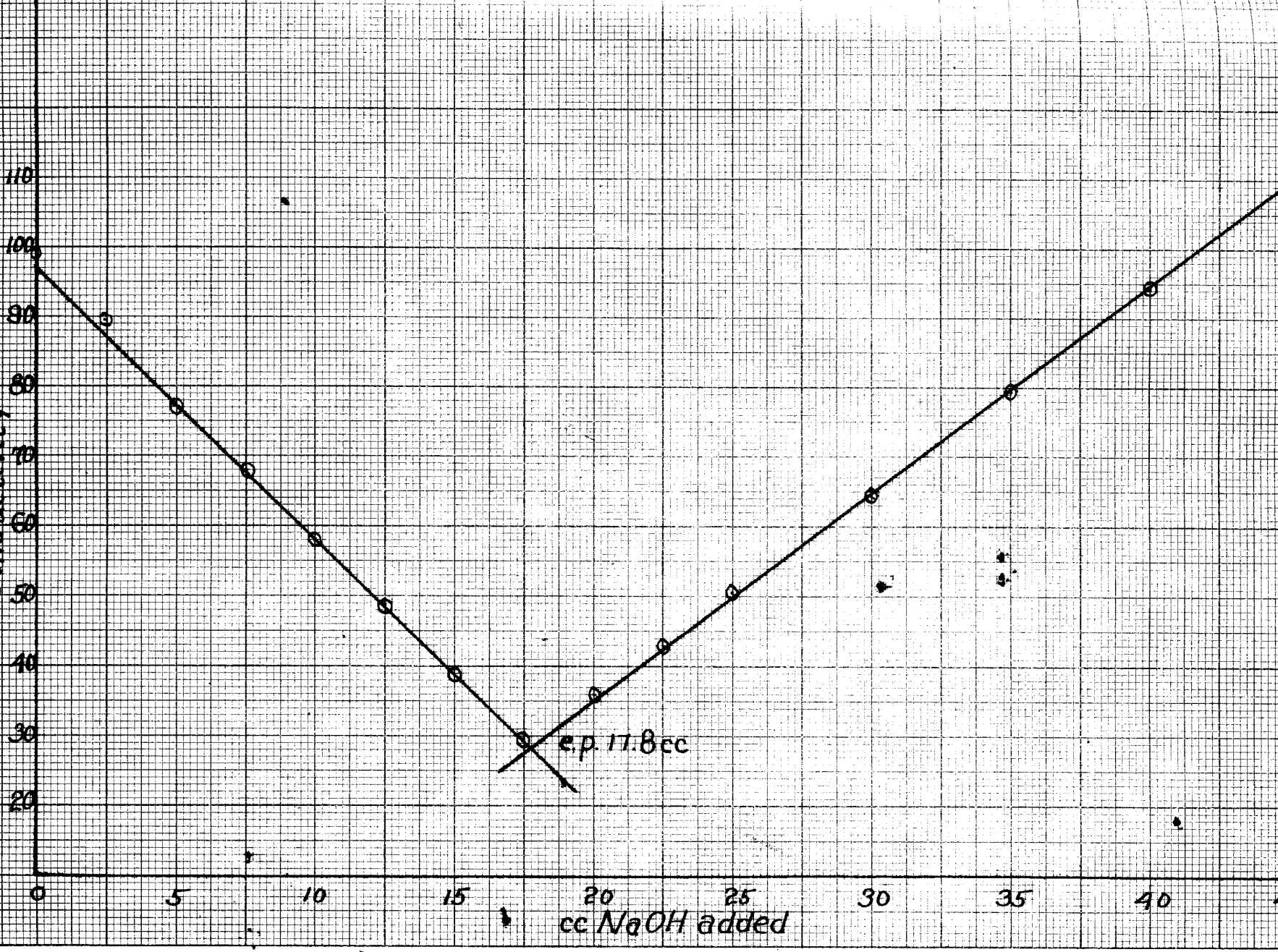
V. TITRATION OF A STRONG ACID WITH A STRONG BASE

During the titration of a strong acid with a strong base the changes in conductance are due to two causes. First, the highly mobile hydrogen ion is replaced by the relatively less mobile cation of the base, e. g. sodium ion, and therefore the resistance will increase. After the equivalence point has been reached, addition of more base merely adds to the electrolyte content of the system and the resistance will then decrease. From these considerations it is evident that the needle should be brought over the left-hand part of the scale before titration has started. Table I shows the data and results for six such titrations done by running in portions of .I2I4-N NaOH into known quantities of .I072-N HCl contained in the titration cell which, as mentioned before, initially contained about 600 cc. of distilled water at room temperature.

The precision is equal to the accuracy with which the graph can be read, about .5%. The accuracy, as far as these data indicate, is of the same order of magnitude, about .5%.

TABLE I

Graph No.	I	2	3	4	5	6
cc. acid	20.0	20.0	20.0	I5.0	I5.I	I5.0
		Conductivity				
cc. base						
0.0	99.0	97.I	99.0	9I.8	9I.8	9I.8
2.0				8I.3	82.8	82.0
2.5	89.2	87.7	89.2			
4.0				7I.5	72.0	7I.5
5.0	77.5	77.0	77.5			
6.0				6I.4	60.4	6I.4
7.5	67.6	67.5	67.6			
8.0				5I.8	52.6	52.I
I0.0	57.8	57.5	58.I	40.7	42.6	42.2
I2.0				32.2	33.3	33.3
I2.5	48.5	48.I	48.5			
I5.0	38.4	38.4	38.6	33.3	32.7	33.3
I7.5	29.4	29.0	29.5			
20.0	35.5	34.6	35.3	5I.8	50.7	5I.5
25.0	50.0	49.3	50.0	70.5	69.4	70.0
30.0	63.7	63.3	63.6	89.3	89.3	88.5
35.0	79.4	78.8	80.6	I09	I08	I08
40.0	93.5	92.5	95.3			
end point	I8.2	I8.2	I8.2	I3.3	I3.4	I3.3
e.p. calc.	I8.2	I8.2	I8.2	I3.3	I3.4	I3.3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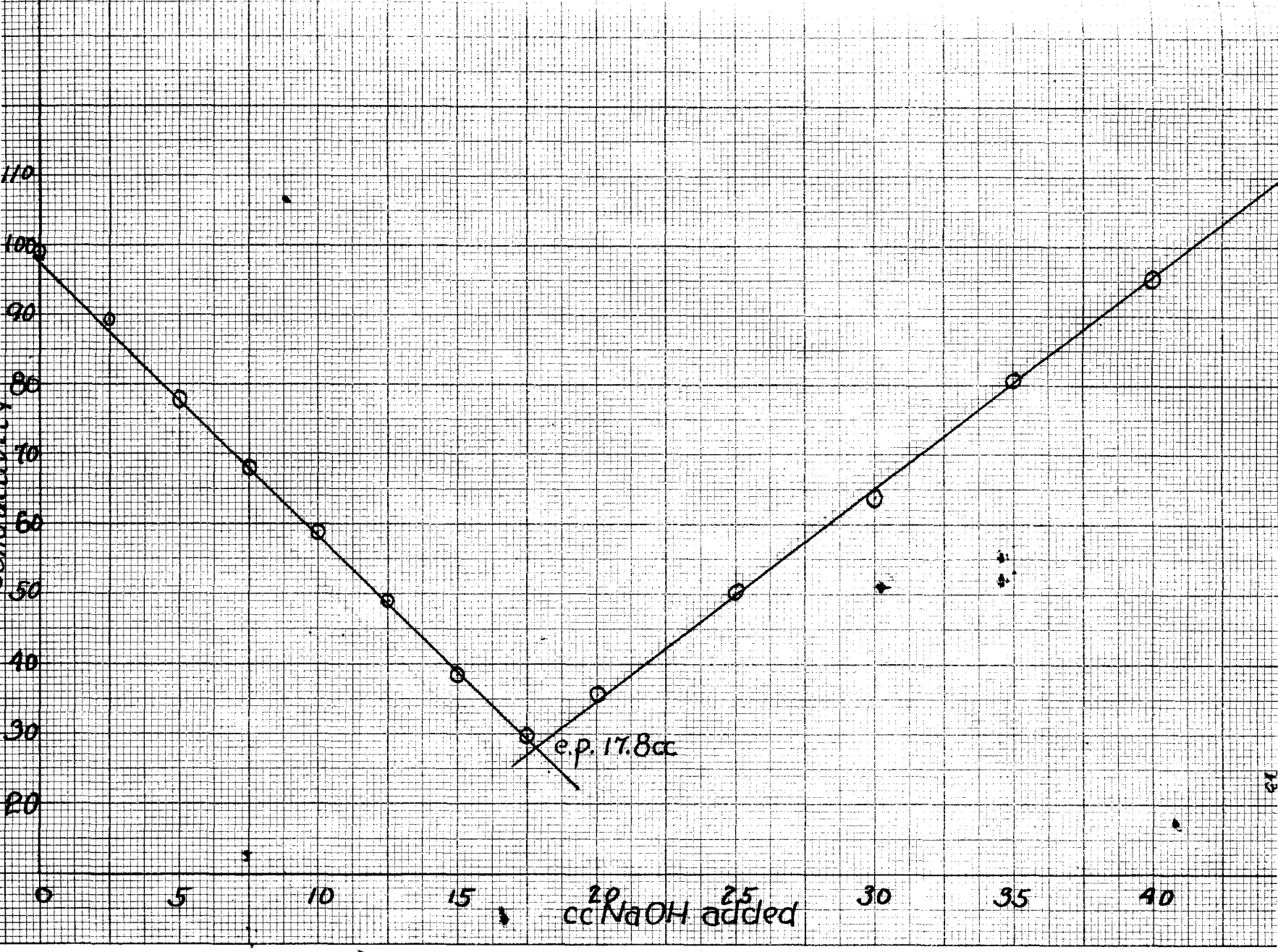
e.p. 17.8cc
cc NaOH added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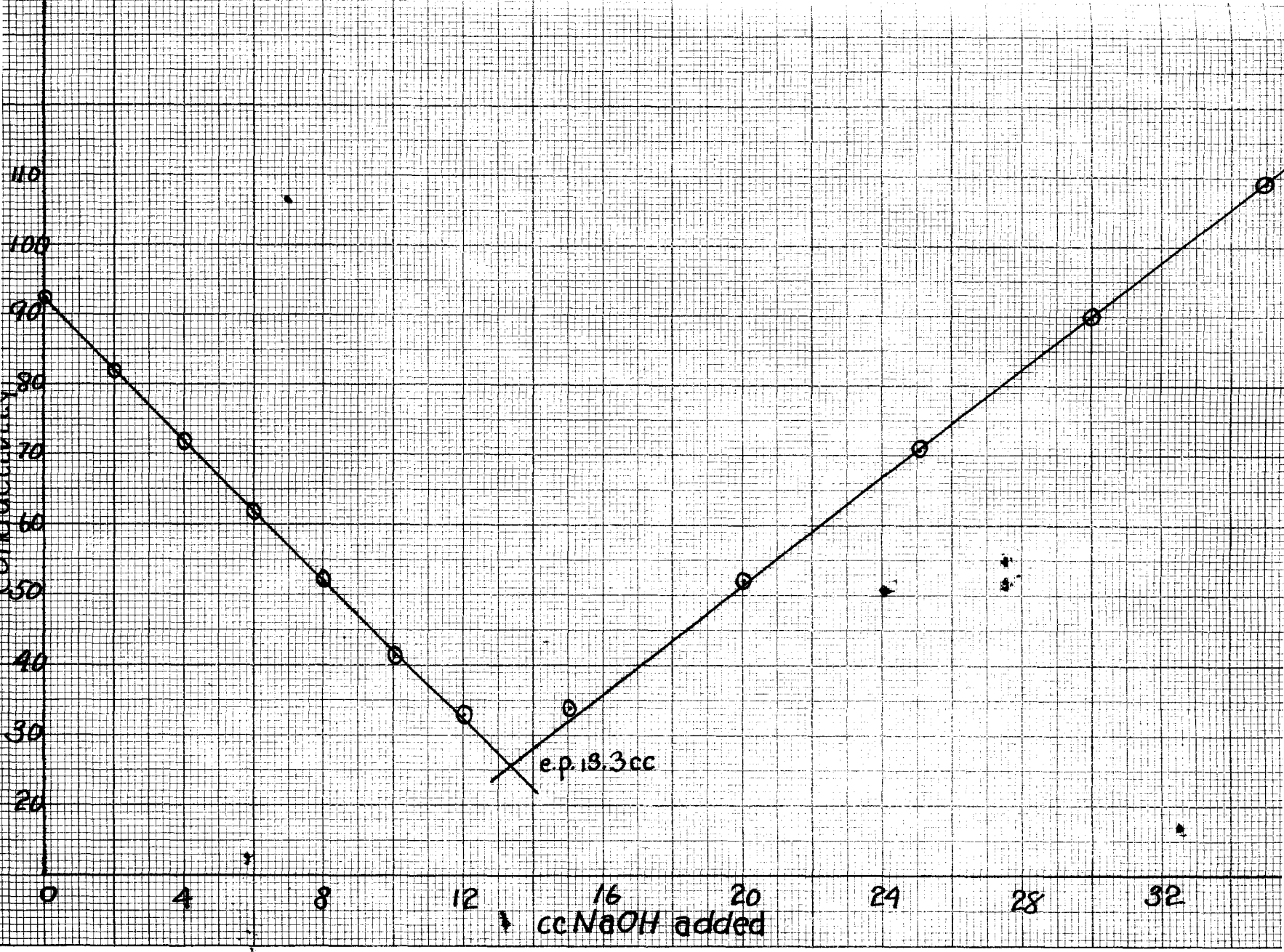
e.p. 17.8cc
cc NaOH added

GRAPH 2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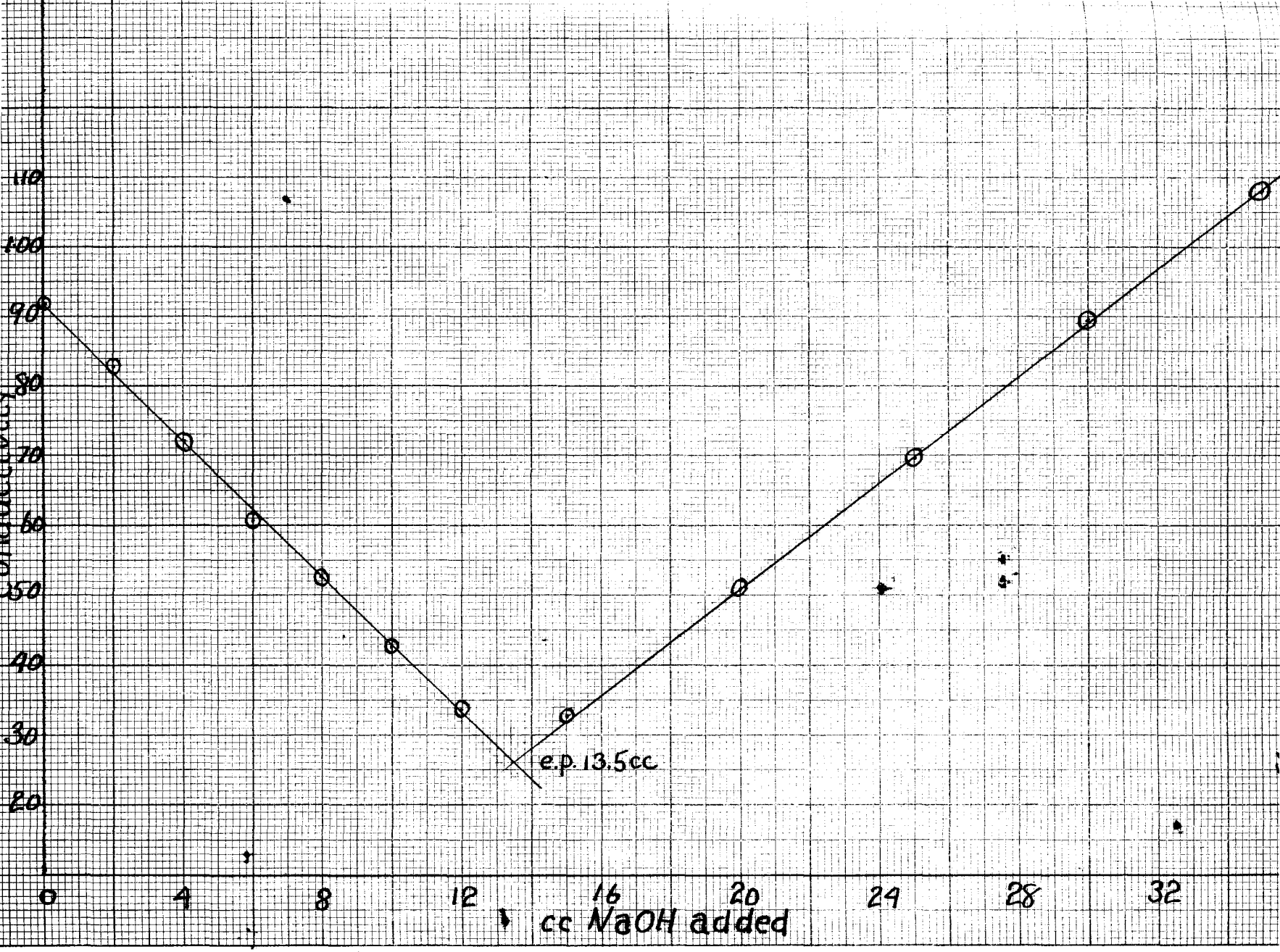
e.p. 13.3 cc
cc NaOH added

GRAPH 4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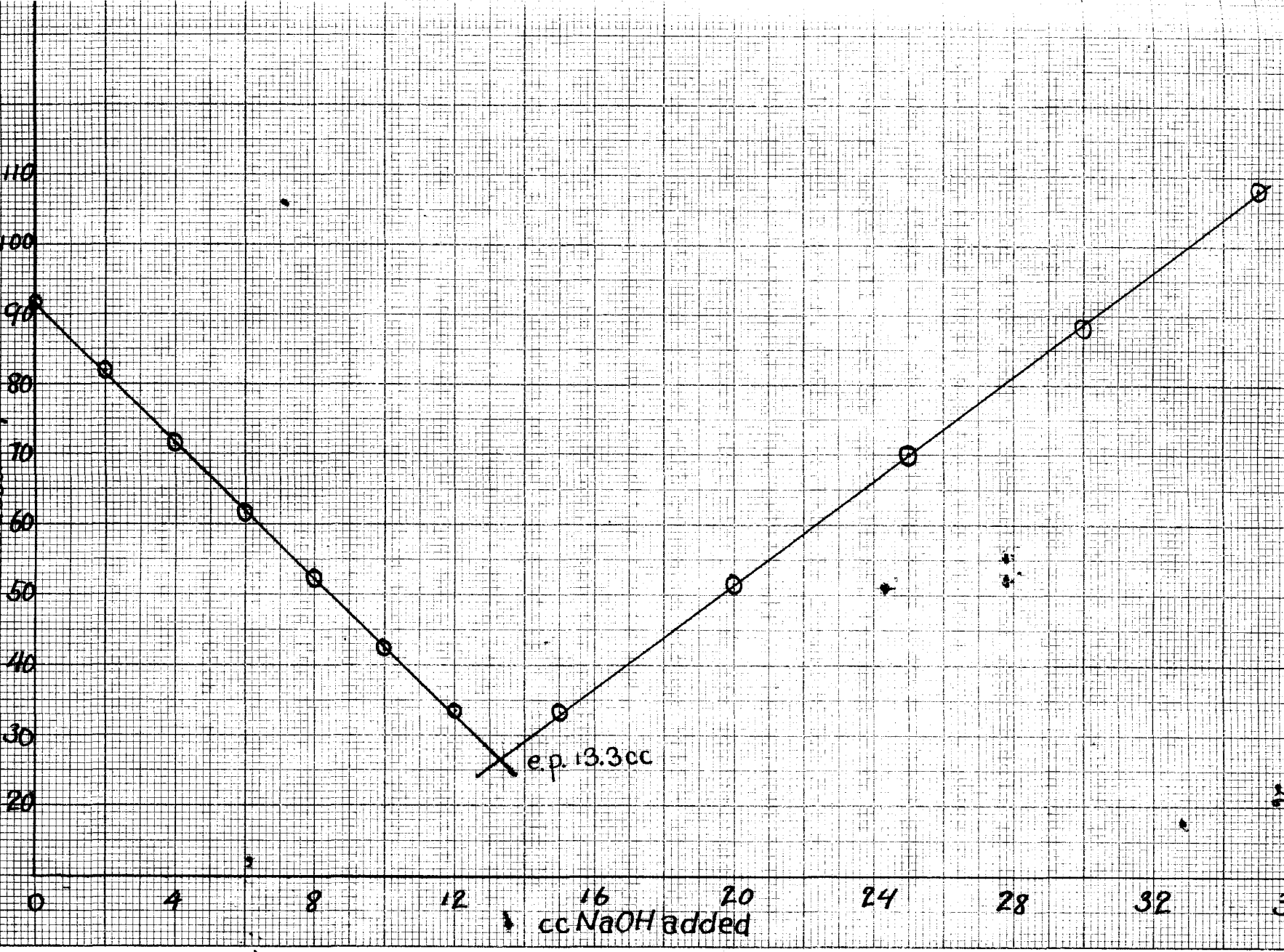
e.p. 13.5cc
cc NaOH added

GRAPH F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e.p. 13.3 cc
cc NaOH added

GRAPH 6

VI. TITRATION OF MIXED ACIDS WITH STRONG BASE

Here an attempt is made to locate twoend points in a mixture of known amounts of acetic and hydrochloric acids when titrated with sodium hydroxide. The strong acid should be neutralized first and the general form of the curve be like the first half of the strong acid - strong base graph. Acetic acid will then be neutralized. The mechanism is different however. Sodium acetate is formed which has a greater conductance than the relatively undissociated acetic acid and the conductance will rise. After the equivalence point for total acid the curve will be as in strong acid - strong base. The mechanism of neutralization is not, unfortunately, quite as simple as stated above. Near the equivalence point for HCl a buffer system of sodium acetate - acetic acid is set up and the fall in conductance will be graded since the hydrogen ion concentration is kept more or less constant. Furthermore the formation of sodium acetate takes place in the presence of NaCl which adds a constant amount of conductance.

Table 2 shows the data and results for four trials. The average deviation fromthe mean for HCl end point is ±.2% and the error is I.7%. The average deviation from the mean for total acid is I% and the error is I0%. The form of the curve checks with both theory and the literature[6].

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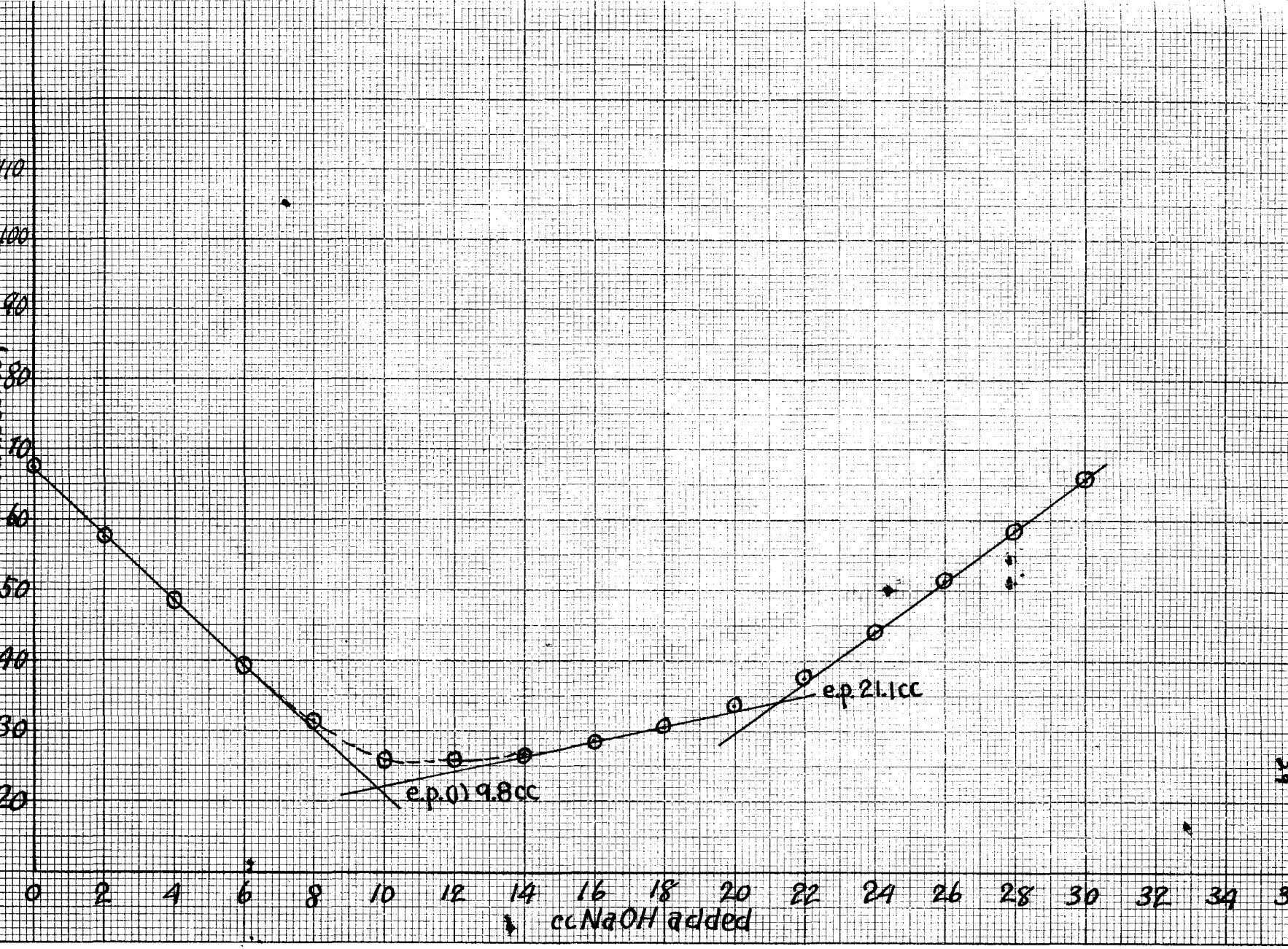
6. Britton, Op. Cit. p.59

TABLE 2

Graph No.	7	8	9	I0
cc. .I2I6-N HOAc	I0.0	I0.0	I0.0	I5.0
cc. .I220-N HCl	I0.0	I0.0	I0.0	I0.0
cc. .I2I4 NaOH	Conductivity			
0.0	67.I	93.4	92.6	98.0
2.0	57.I	79.4	80.6	83.4
3.0	48.3	66.2	66.7	69.9
6.0	39.I	54.3	54.3	58.I
8.0	3I.2	42.9	43.I	45.6
I0.0	25.9	42.9	35.6	37.8
I2.0	25.3	34.0	34.5	36.0
I4.0	26.4	35.7	36.I	37.3
I6.0	28.3	38.3	38.8	40.0
I8.0	30.8	4I,3	4I.6	43.I
20.0	33.6	44.4	45.5	46.I
22.0	37.7	50.8	5I.8	50.0
24.0	44.0	58.8	59.9	52.9
26.0	5I.5	68.5	70.0	56.5
28.0	58.2	78.7	79.4	65.8
30.0	65.8	88.4	90.0	75.8
32.0	7I.9	97.I	98.8	84.0
34.0				95.2
end point HCl	9.7	9.7	I0.I	I0.0
end point total acid	20.8	2I.2	2I.4	25.5
e.p. HCl calc.	I0.0	I0.0	I0.0	I0.0
e.p. total acid calc.	20.0	20.0	20.0	25.0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e.p. 21.1cc
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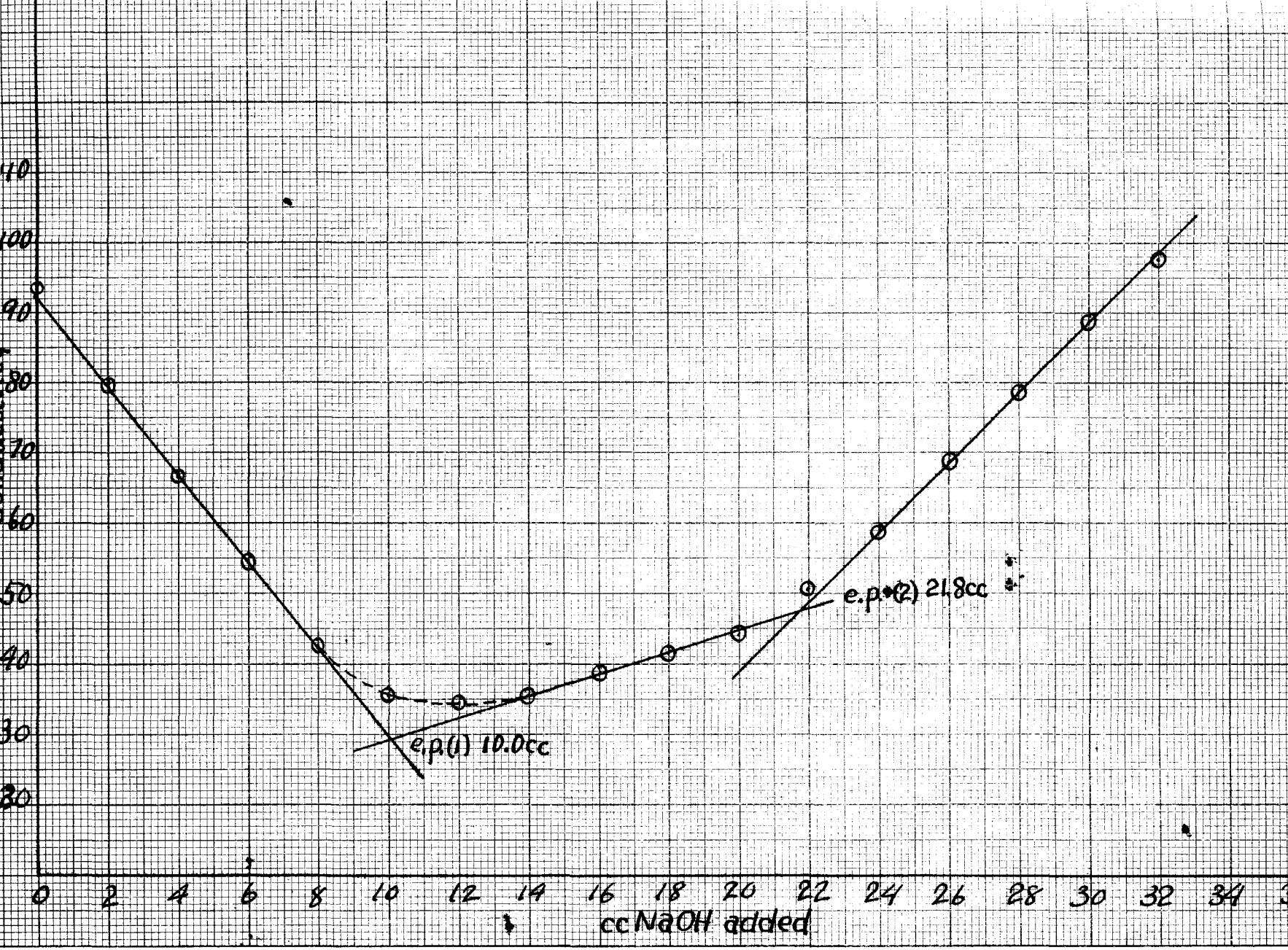
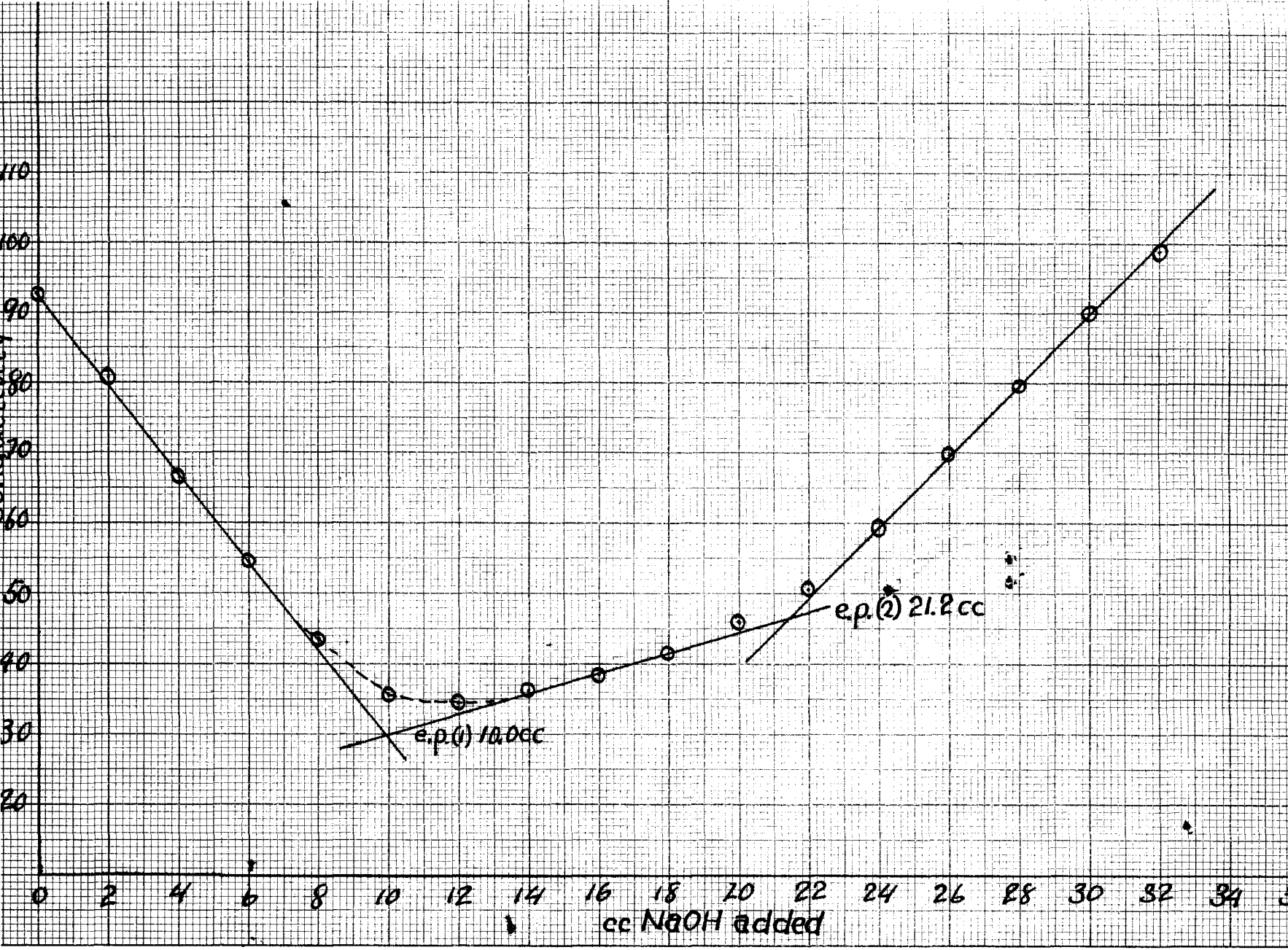
cc NaOH added

GRAPH 7



GRAPH 8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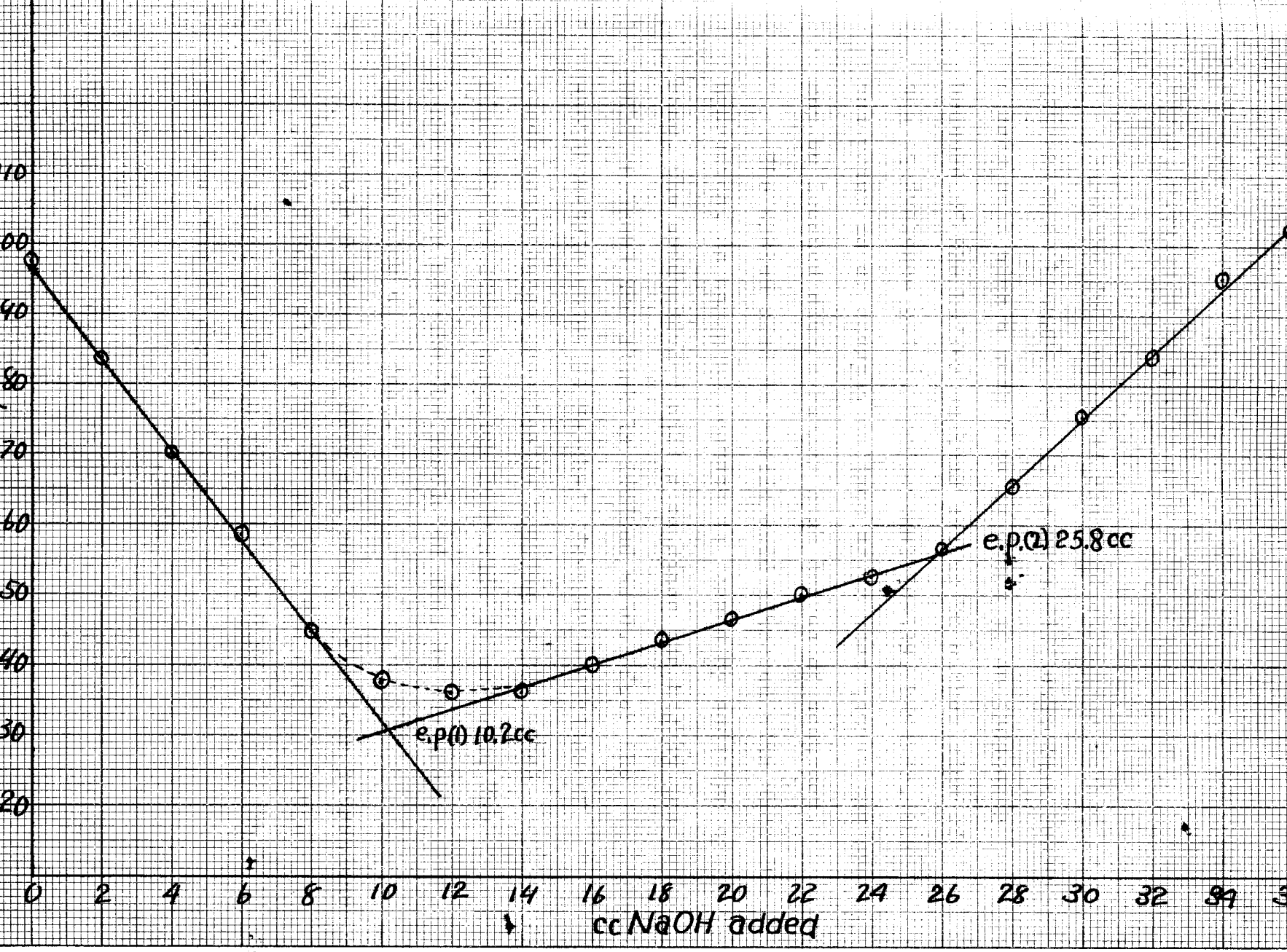
e.p.(1) 10.0cc
e.p.(2) 21.2 cc
cc NaOH added

GRAPH 9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32
e.p.(1) 25.8 cc
e.p(1) 10.2cc
cc NaOH added

GRAPH 10

VII. TITRATION OF A WEAK ACID WITH A WEAK BASE

Here the full value of the conductometric method of titration is brought out. It is very difficult to titrate a weak acid with a weak base by means of an indicator because of the buffer systems set up on either side of the equivalence point. Conductometrically, however, the end point is as sharply defined as in most titrations and may be located with a rather high degree of accuracy.

The system used in acetic acid titrated with ammonium hydroxide. As ammonium acetate is formed by addition of base, the conductivity will rise since the highly ionized salt replaces the slightly ionized acid. After the stoichometric point is reached, further additions of bases contributes practically nothing to the total conductivity since ammonium hydroxide is so weak. The general form may then be predicted and, as the graphs show, are in keeping with fact.

Table 3 shows the data and results for four titrations of .I2I6-N HOAc with .I420-N NH_4OH. The average deviation from the mean is .8% and the error is 2.3%. Britton shows the same form of curve[7].

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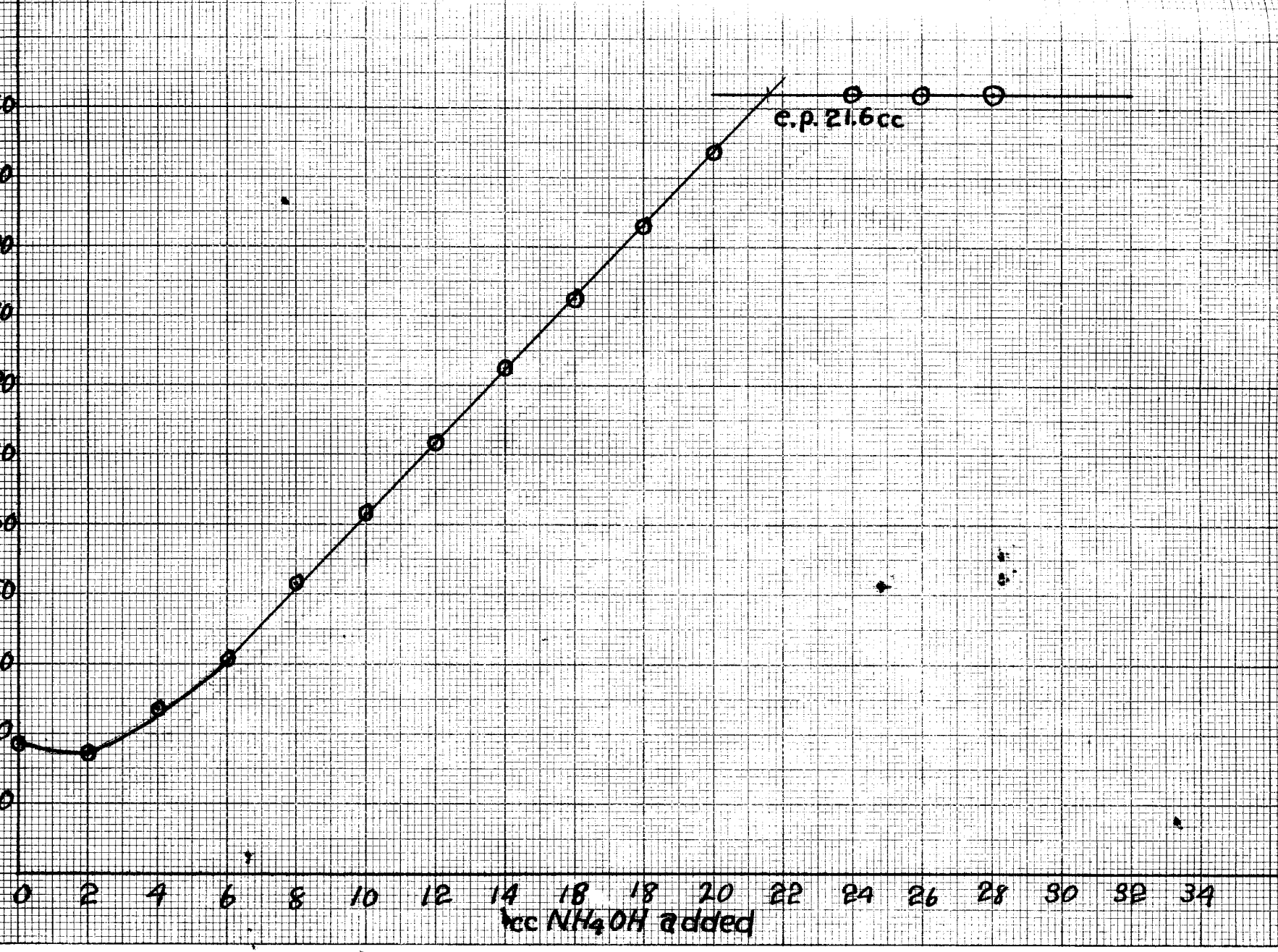
7. Britton, Op. Cit. p. 59

TABLE 3

Graph No.	II	I2	I3
cc. acid	25.0	25.0	25.0
cc. base	Conductivity		
0.0	28.6	25.9	26.0
2.0	27.0	23.8	23.8
4.0	33.2	28.6	28.6
6.0	4I.5	36.8	36.8
8.0	5I.8	45.2	45.2
I0.0	6I.4	54.4	54.0
I2.0	7I.9	62.9	62.9
I4.0	82.6	73.0	72.4
I6.0	92.6	8I.9	8I.9
I8.0	I03	90.9	9I.6
20.0	II4	I00	I00
22.0	I22	I09	I09
24.0	I22	I09	II0
26.0	I22	I09	II0
28.0	I22	I09	II0
end point	2I.6	2I.8	22.2
e.p. calculated	2I.4	2I.4	2I.4

NOTE: ANY DISCREPANCY BETWEEN TABULATED DATA AND GRAPHS SHOULD ALWAYS BE REFERRED TO TABULATED DATA FOR CORRECT VALUES.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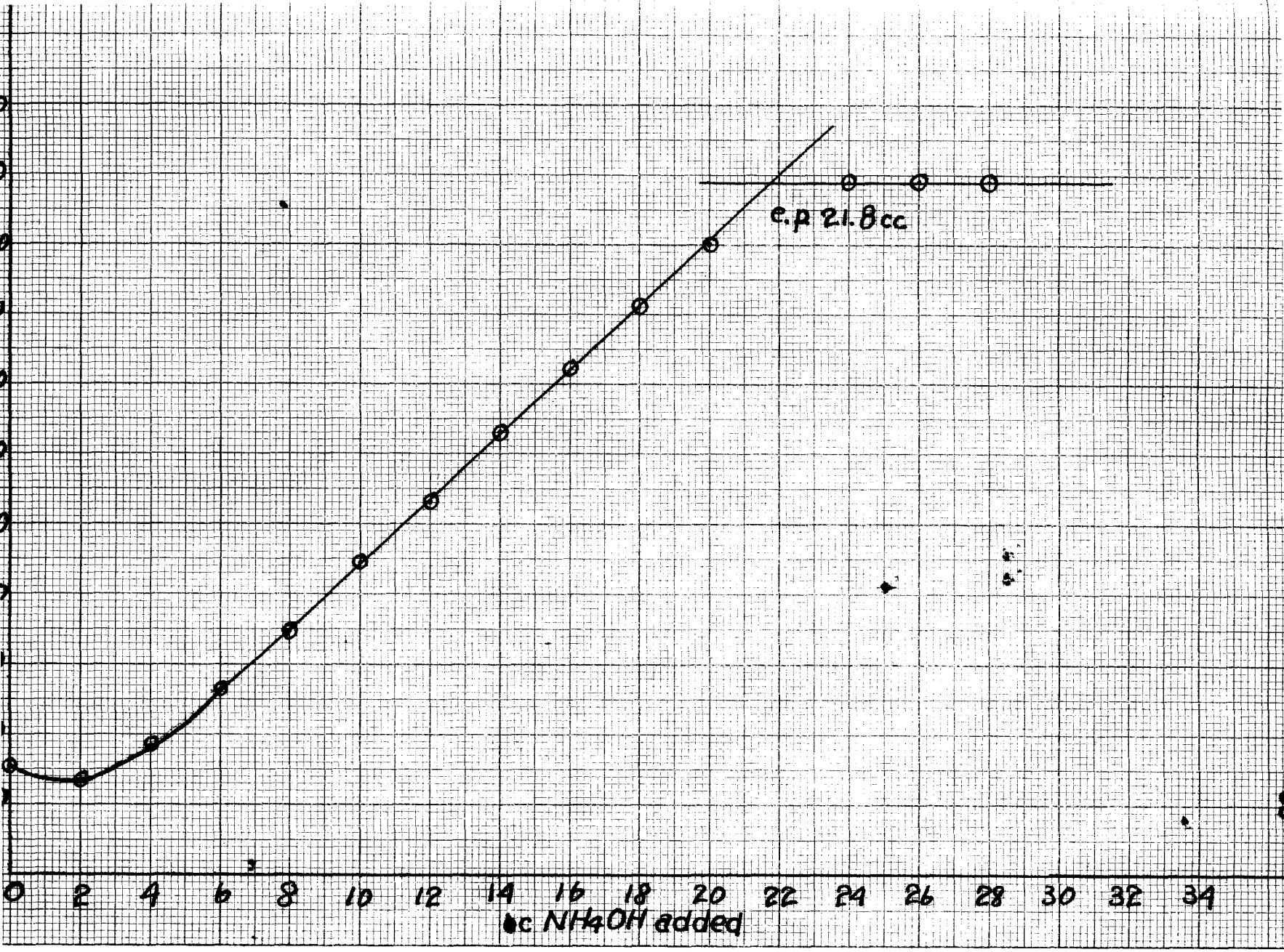
cc NH_4OH added

GRAPH II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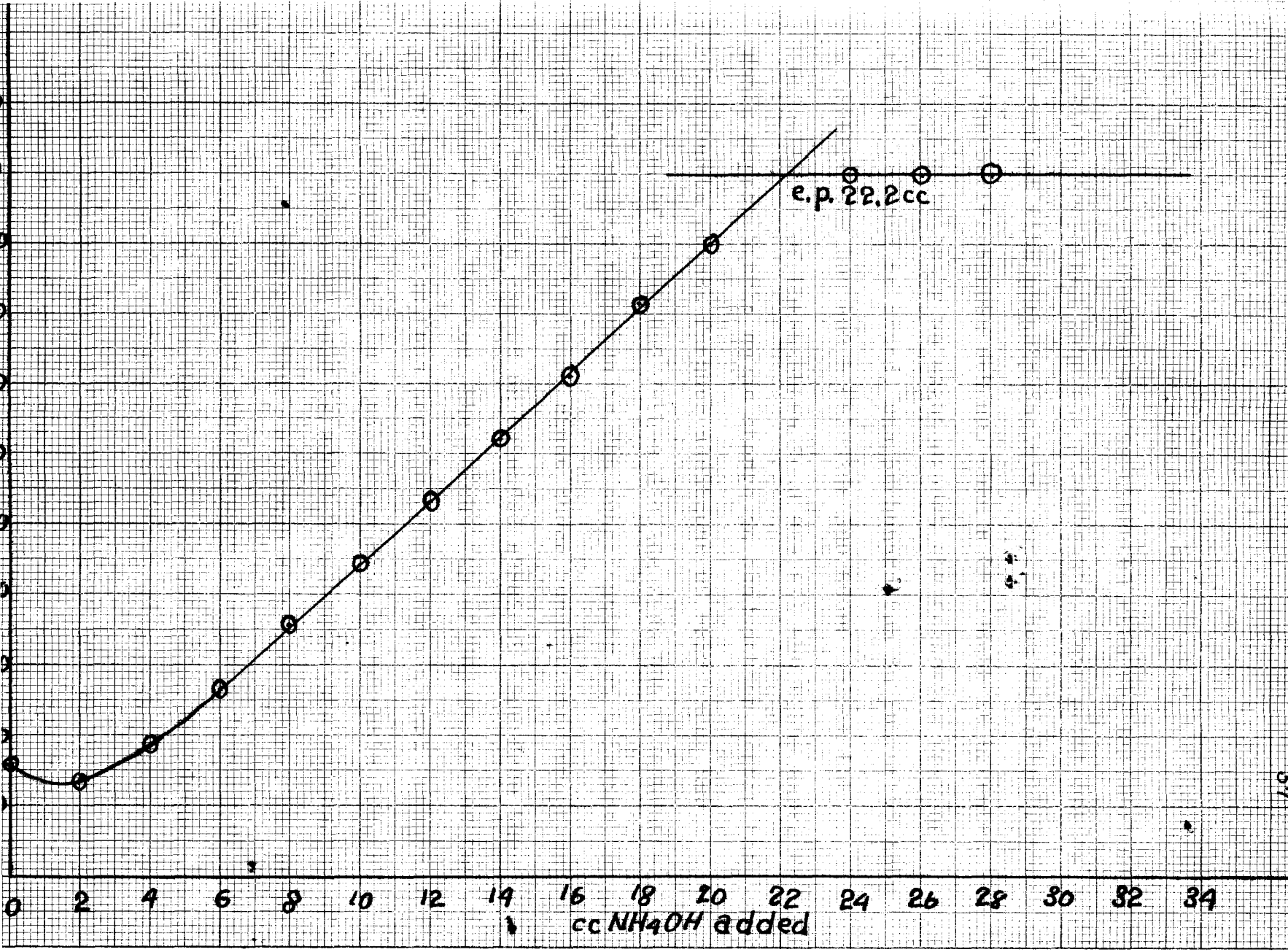
30
32
34
cc NH4OH added

GRAPH 12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10
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14
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18
20
22
24
26
28
30
32
34
cc NH4OH added

GRAPH 13

VIII. ANALYSIS OF UNKNOWN SODA ASH

When sodium carbonate is titrated with HCl the carbonate is first converted into the bicarbonate. This point may be determined with phenolphthalein, but is not definite because of the buffer system set up. When a carbonate is titrated conductometrically we might expect the following form of curve. As acid is added, one carbonate ion is converted into a bicarbonate ion and a chlodide ion added. Since the conductances of these three ions are all about the same, we would expect little or no change in conductance. After the bicarbonate point, further additions of acid cause the formation of water and carbon dioxide from the bicarbonate. The equivalent reaction is the substituting of chloride ion for bicarbonate ion and, since these conductances are about equal, we might expect an extended straight line from the previous line. However, the solubility of CO_2 varies as the pH of the solution, and hence we shall have a small amount of CO_2 in solution and in equilibrium with bicarbonate ion, at least until enough acid is added to minimize the solubility of CO_2. Thus we can see that, although we predetermined the shape of the curve, we cannot predetermine the exact drawing of the curve. Graph I4 shows the results of titrating anhydrous sodium carbonate. I4-A shows the lack of accuracy when a conventional modulus is chosen, and I4-B the increased accuracy with an increased ordinate-modulus. (See page I9, H)

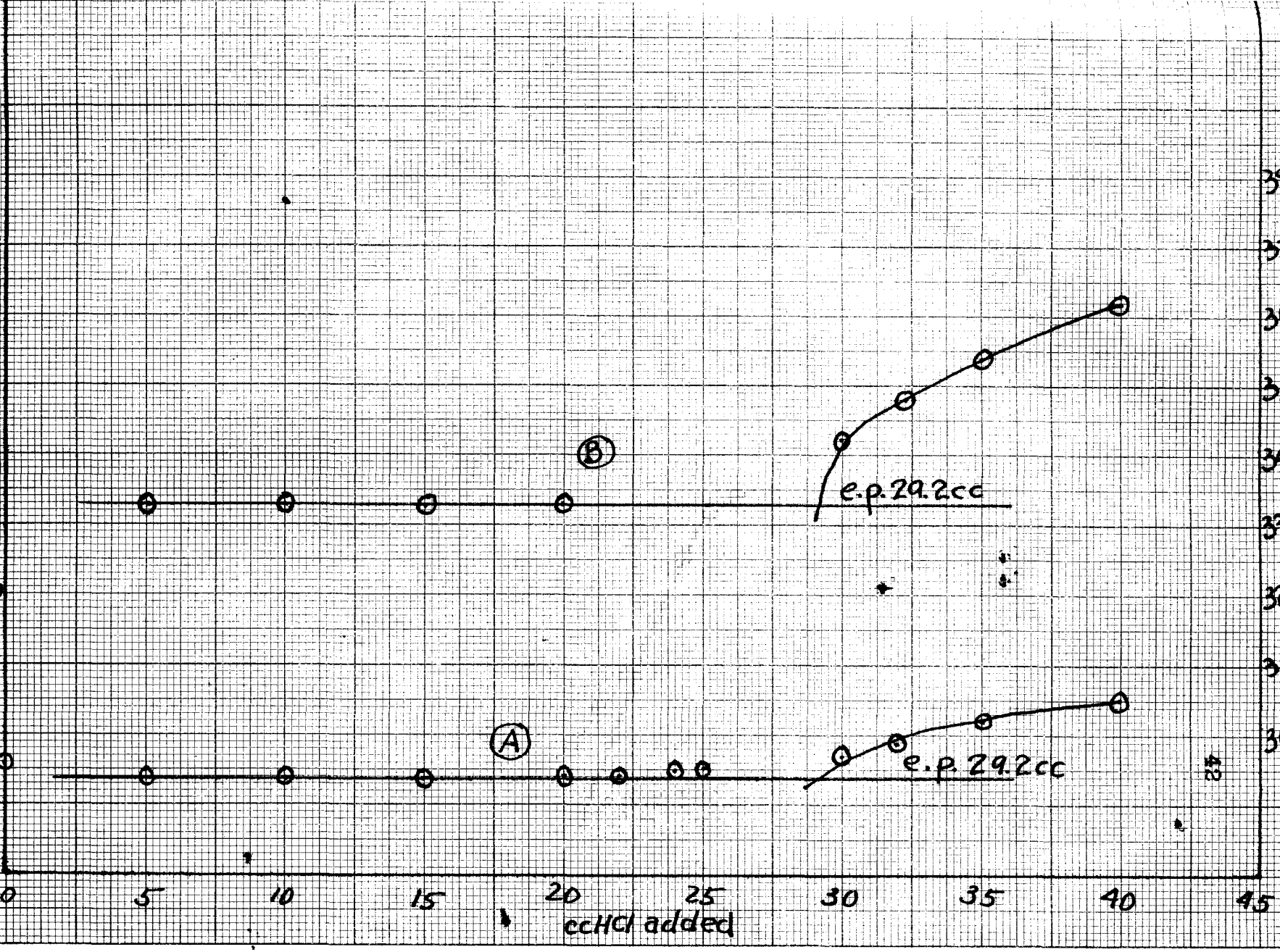
Table 4 shows the results of titration of samples of soda ash with .6900-N HCl. The accepted percent Na_2CO_3 for this sample is 76.3%. The average deviation from the mean for the results is I% and the error is .3%

TABLE 4

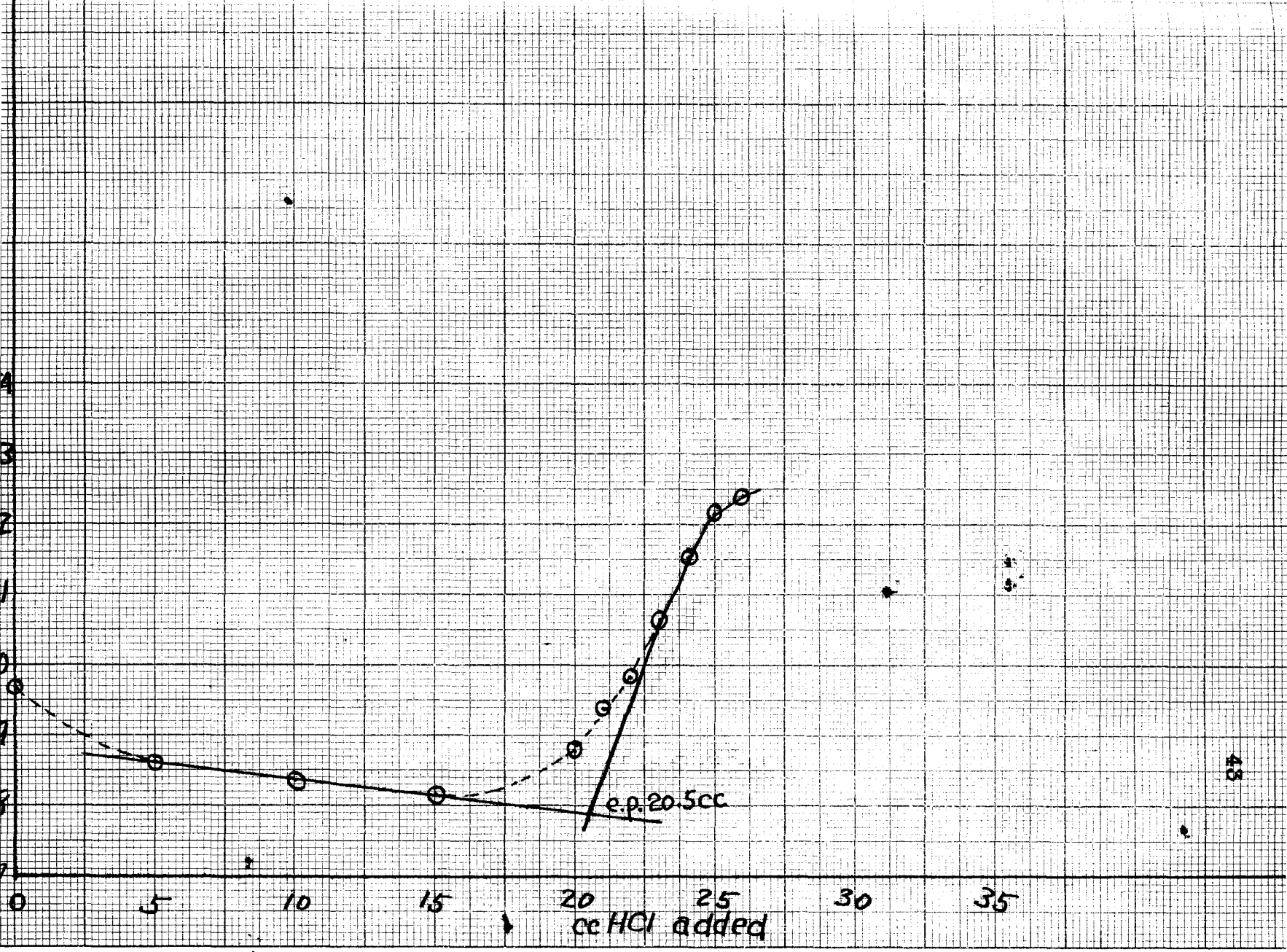
Graph No.	I4	I5	I6	I7
gm. Anh.Na_2CO_3	2.I5I			
gm. soda ash		I.9985	2.0545	I.9987
cc. acid	Conductivity			
0.0	33.9	49.7	52.I	50.7
5.0	33.3	48.6	50.7	5050
I0.0	33.3	48.3	50.0	49.7
I5.0	33.3	48.I	50.5	50.0
20.0	33.3	48.7	50.7	50.0
2I.0		49.3		
22.0	33.4	49.7		50.3
23.0		50.5	52.4	5I.2
24.0	33.6	5I.5	52.6	5I.8
25.0	33.6	52.3	53.2	52.4
26.0		52.3	53.4	
27.0			54.4	52.9
28.0		52.9	54.9	
30.0	34.2	53.7	54.9	53.5
32.0	34.8			
35.I	35.4			

TABLE 4 (continued)

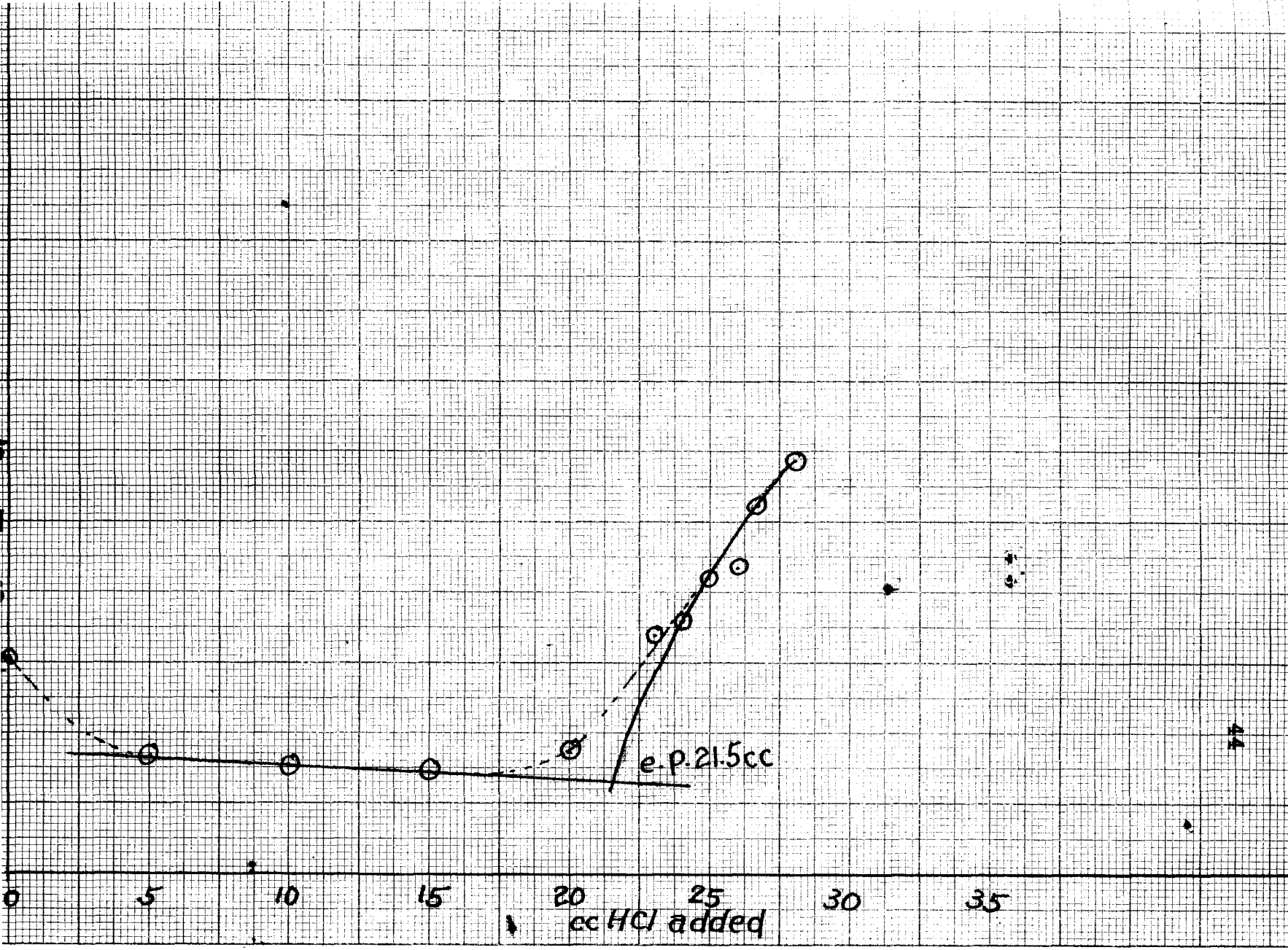
	I4	I5	I6	I7
40.0	36.2			
end point	29.2	20.5	2I.5	2I.0
cc. acid/gm.sample	I3.6	I0.3	I0.5	I0.5
% Na_2CO_3 calculated	99.5	75.0	76.5	76.8
average % in soda ash			76.2	



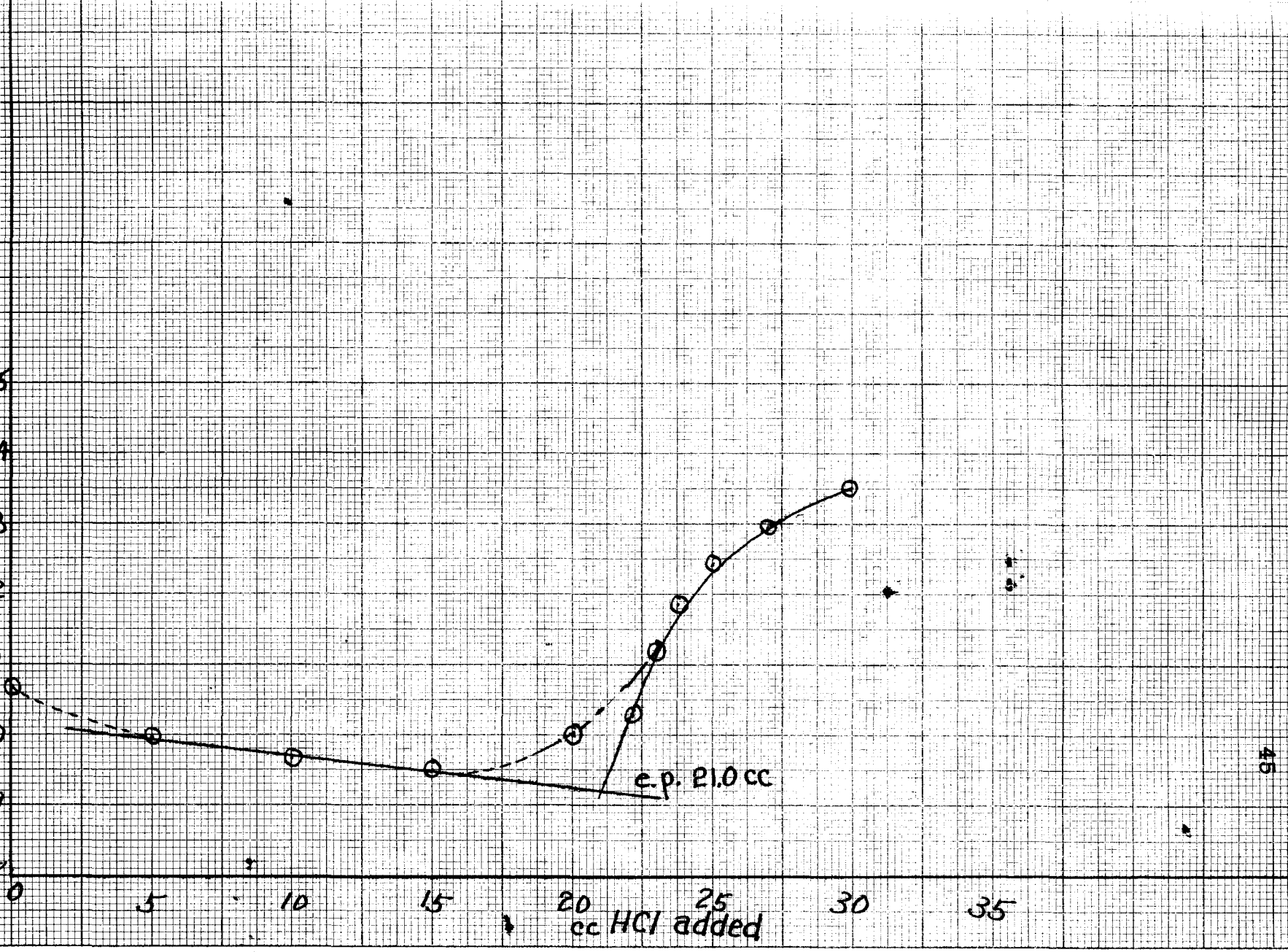
GRAPH 4



GRAPH 15



GRAPH 16



GRAPH 17

IX. TITRATION OF SULPHATE WITH BARIUM CHLORIDE

As a solution of any sulphate is titrated with barium chloride, sulphate ion is removed by precipitation as barium sulphate and for every sulphate removed two chloride ions are added to the solution. Since the limiting equivalent conductances of the chloride ion to $\frac{1}{2}$ sulphate is as 65 is to 68, we might expect very little, if any, change in conductance up to the equivalence point.

The necessity of considering a time factor after the addition of reagent is most pronounced in this titration. After the addition of a small amount of reagent, the needle first indicates a decrease in resistance and then slowly swings back to about its initial position. This seems to indicate a low precipitation velocity for barium sulphate or, perhaps, a heat effect. The time necessary for the needle to come to equilibrium varies with the amount of reagent added. In general the greatest time factor is for the first few additions of reagent. The maximum time necessary for the establishment of equilibrium was foundto be about three minutes.

Table 5 shows the data and results of standardization of Barium chloride solution against anhydrous $Na_2 SO_4$ and runs on a soluble sulphate sample. Table 6 shows the data and results of titration of measured amounts of .200-N sulphate against the standardized barium solution.

TABLE 5

Graph No.	I8	I9	20	2I	22	23	24
gm. anh. Na_2SO_4	.2I69	.I762	.II93	.I7I8			
gm. sample					.2744	.2586	.2520
cc. $BaCl_2$	Conductivity						
0.0	55.3	50.2	58.2	52.I	50.7	54.7	52.4
4.0	57.8		60.3				
5.0		50.0		50.0	50.7	54.7	52.6
8.0	57.8			59.5			
I0.0		50.0		50.0	50.7	54.7	52.6
I2.0	57.8		58.9				
I5.0		50.0		50.0	50.7	54.7	52.6
I6.9	57.8		60.9				
20.0	57.8	50.0	67.6	50.0	50.7	54.7	52.6
22.0			78.I				
22.5				5I.3			
24.0	58.5		84.8				
25.0		52.I		53.8	5I.3	56.2	54.I
27.5		55.6		57.8			
28.0	59.2		99.0				
30.0	6I.4	59.9		59.9	54.6	6I.7	59.5
32.0	64.5						
32.5		63.3		65.4			
34.0	68.0						
35.0		67.6		69.9	58.8	67.6	65.0

TABLE 5 (continued)

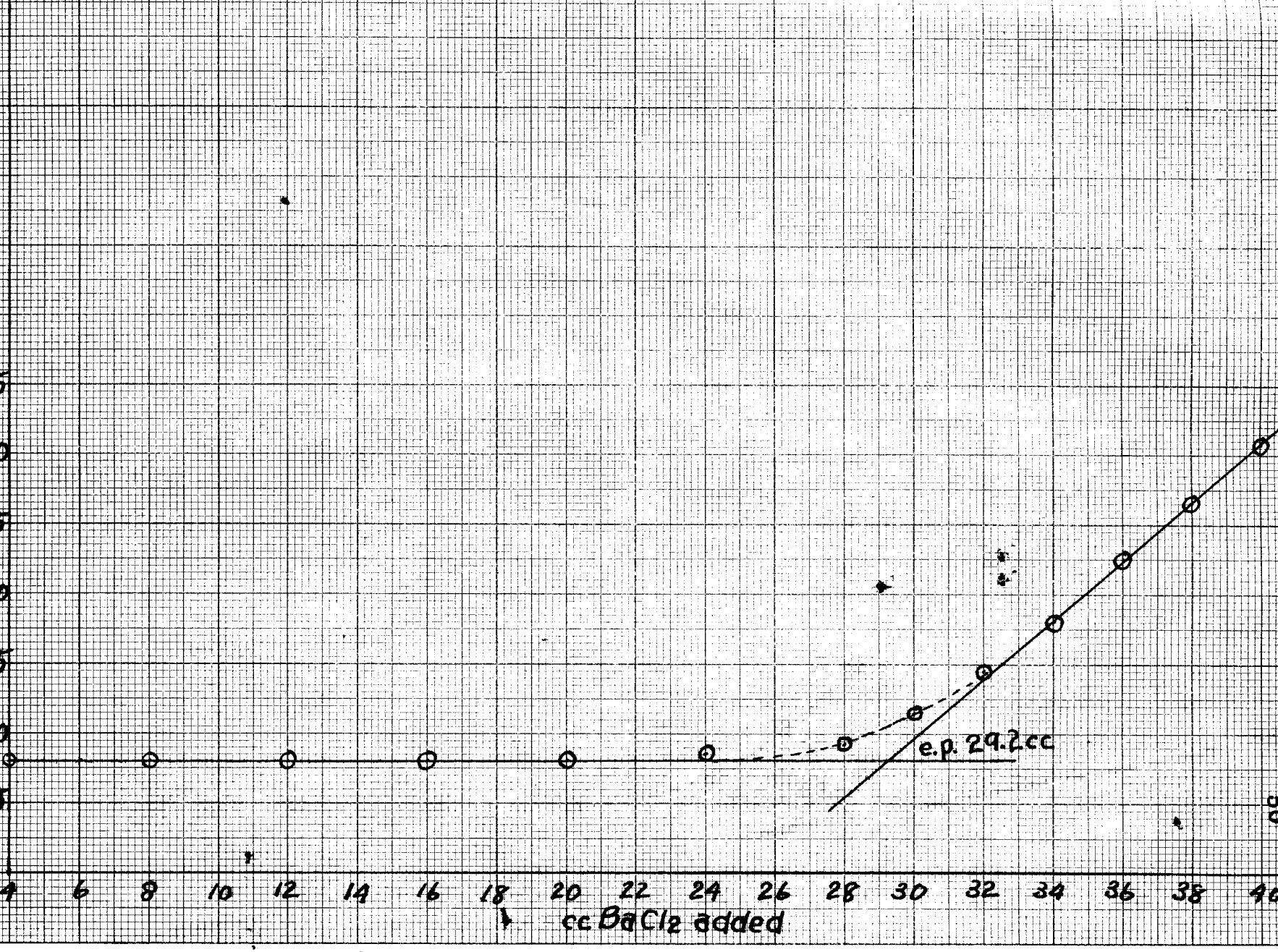
	I8	I9	20	2I	22	23	24
36.0	72.5						
37.5		7I.5		75.2			
38.0	76.4						
40.0	80.6	75.4			63.3	74.6	7I.9
42.0	84.0						
45.0					68.0	79.9	76.9
50.0					73.0	85.5	82.7
end point	29.2	24.2	I6.4	23.6	27.0	24.5	24.5
cc/gm	I34.7	I37.2	I37.2	I37.3	98.3	94.7	97.3
average cc/gm	I37.2				96.8		
Normality, calc.	.I025						
% SO_3, calc.					39.7		
% SO_3, accepted					37,2		

The precision for the standardization is the accuracy with which the graph may be read, about .5%. For the soluble sulphate sample, the average deviation from the mean is 2% and the error is 6.5%. This is not as good as the precision for the standarization, and therefore more sulphate determinations were made. (Table 6)

TABLE 6

Graph No.	25	26	27	28	29	30	3I	32	33
cc. .2N SO_4	20.0	I9.0	I8.0	I7.0	I6.0	I5.0	I4.0	I3.0	I2.0
cc. $BaCl_2$				Conductivity					
0.0	40.0	40.0	40.0	42.8	43.8	45.8	43.3	43.5	43.5
2.0	4I.7								
4.0	38.4	40.0	40.0	42.8	43.8	45.8	43.6	43.8	43.5
6.0	4I.3								
8.0	4I.3	38.0	40.5	42.6	43.8	45.8	43.7	43.8	43.5
I2.0	4I.3	38.0	40.5	42.6	43.7	45.8	44.0	44.3	43.4
I6.0	4I.6	38.0	40.0	42.4	43.7	45.8	44.3	44.I	43.5
20.0	4I.7	38.2	40.5	42.4	43.8	45.8	44.6	45.0	43.9
24.0	4I.5	38.2	4I.2	42.2	43.8	46.3	45.0	46.5	45.7
28.0	4I.5	38.4	4I.5	42.2	44.9	47.7	47.6	5I.3	52.6
32.0	4I.5	42.0	43.5	43.5	47.0	52.0	52.5	55.7	57.8
36.0	42.0	44.5	47.4	47.4	5I.5	56.I	58.I		
40.0	43.7	4I.5	47.8	52.4	55.4	6I.4	63.6		
44.0	46.9	45.0	52.I	56.8	60.2				
48.0	50.7	49.5	55.8	6I.8					
50.0	52.4	5I.2							
end point	38,4	37.6	32.5	3I.8	29.I	25.8	26.0	22.0	2I.6
e.p. calc. for ccBa/ccSO_4	I.92	I.98	I.80	I.87	I.82	I.72	I.86	I.69	I.80
average e.p. in ccBa/cc sulphate					I.83				

Average dev. from mean is 3.8%. Variables are unknown.


e.p. 29.2cc
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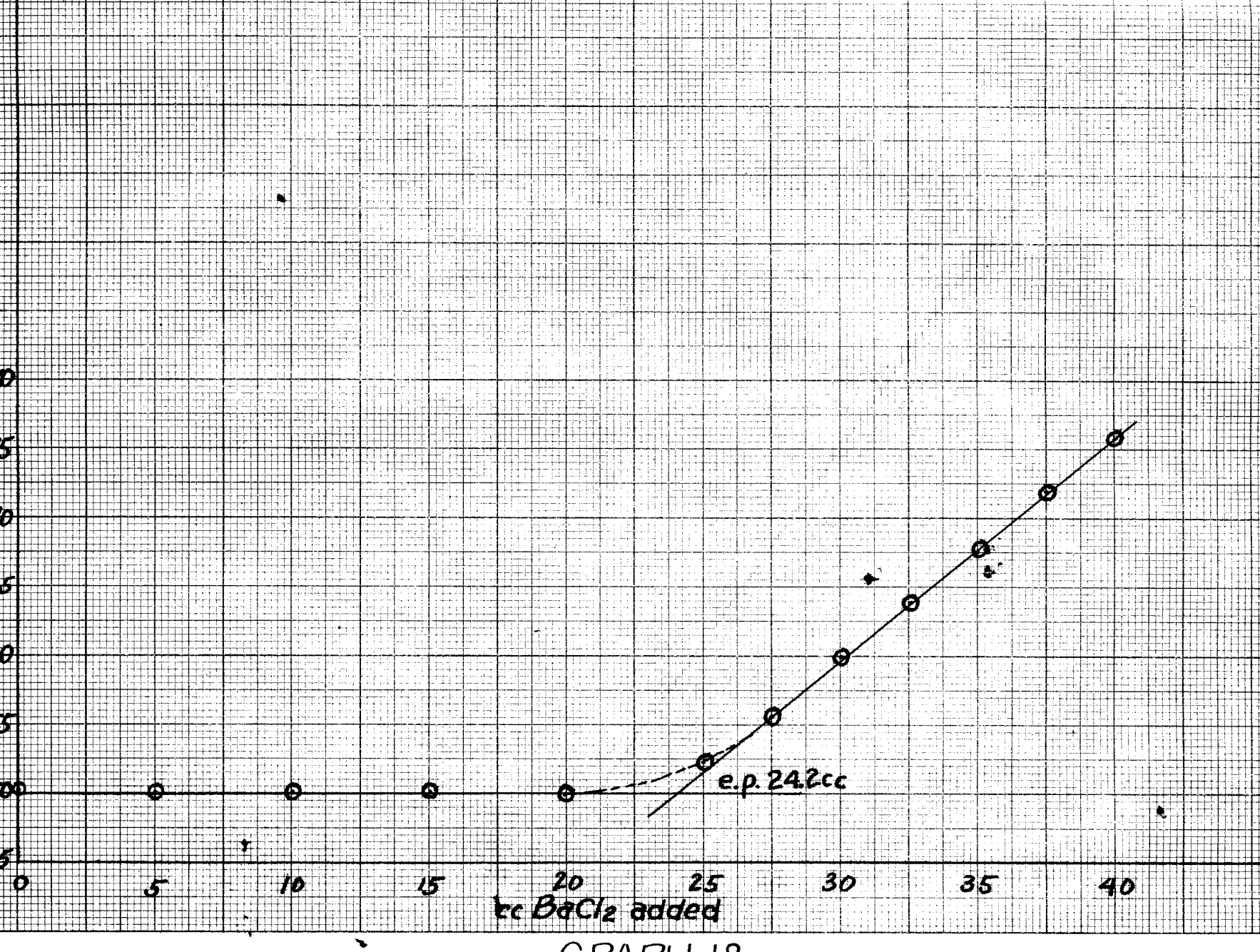
34
36
38
cc BaCl2 added

GRAPH 18



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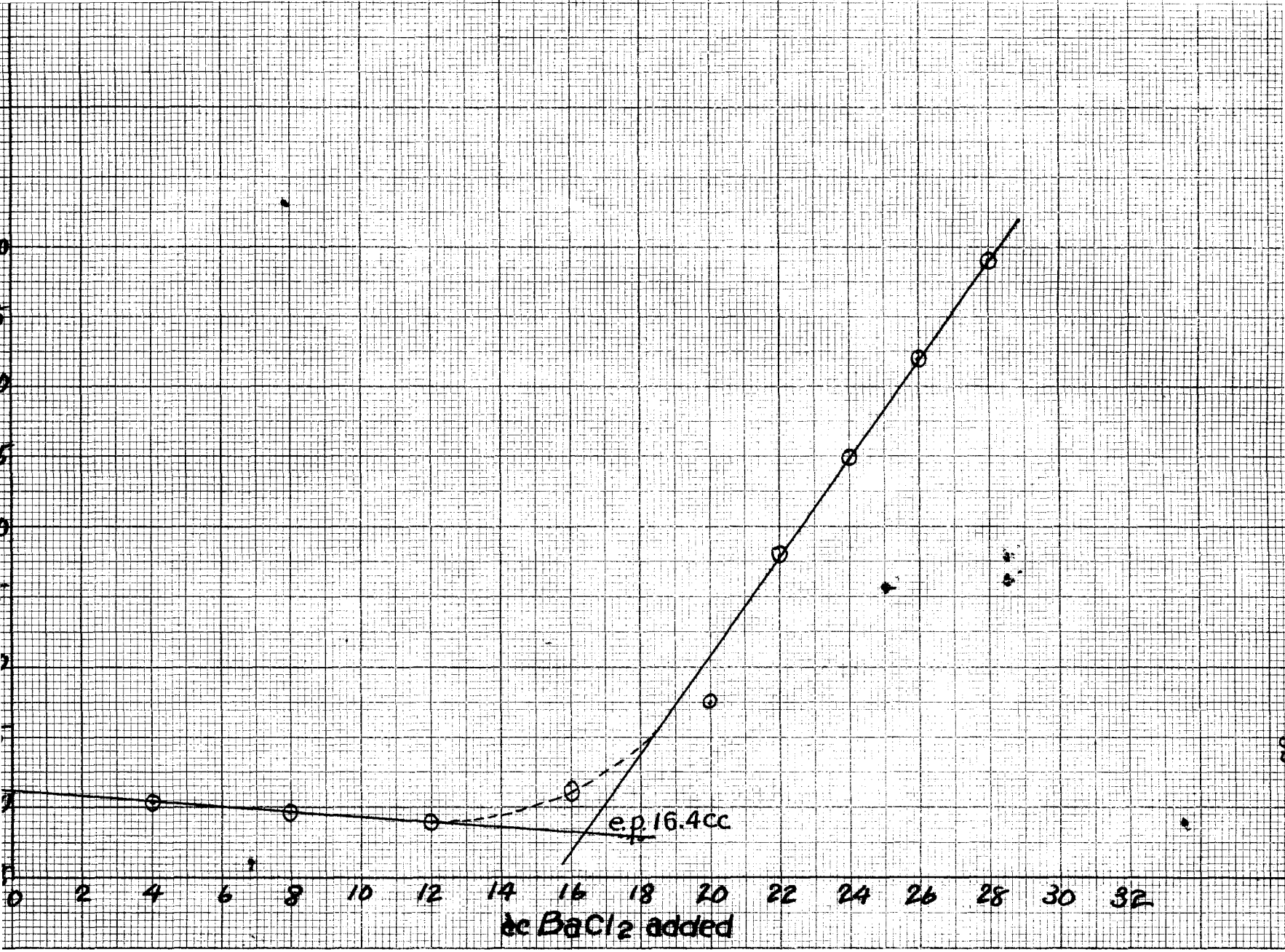

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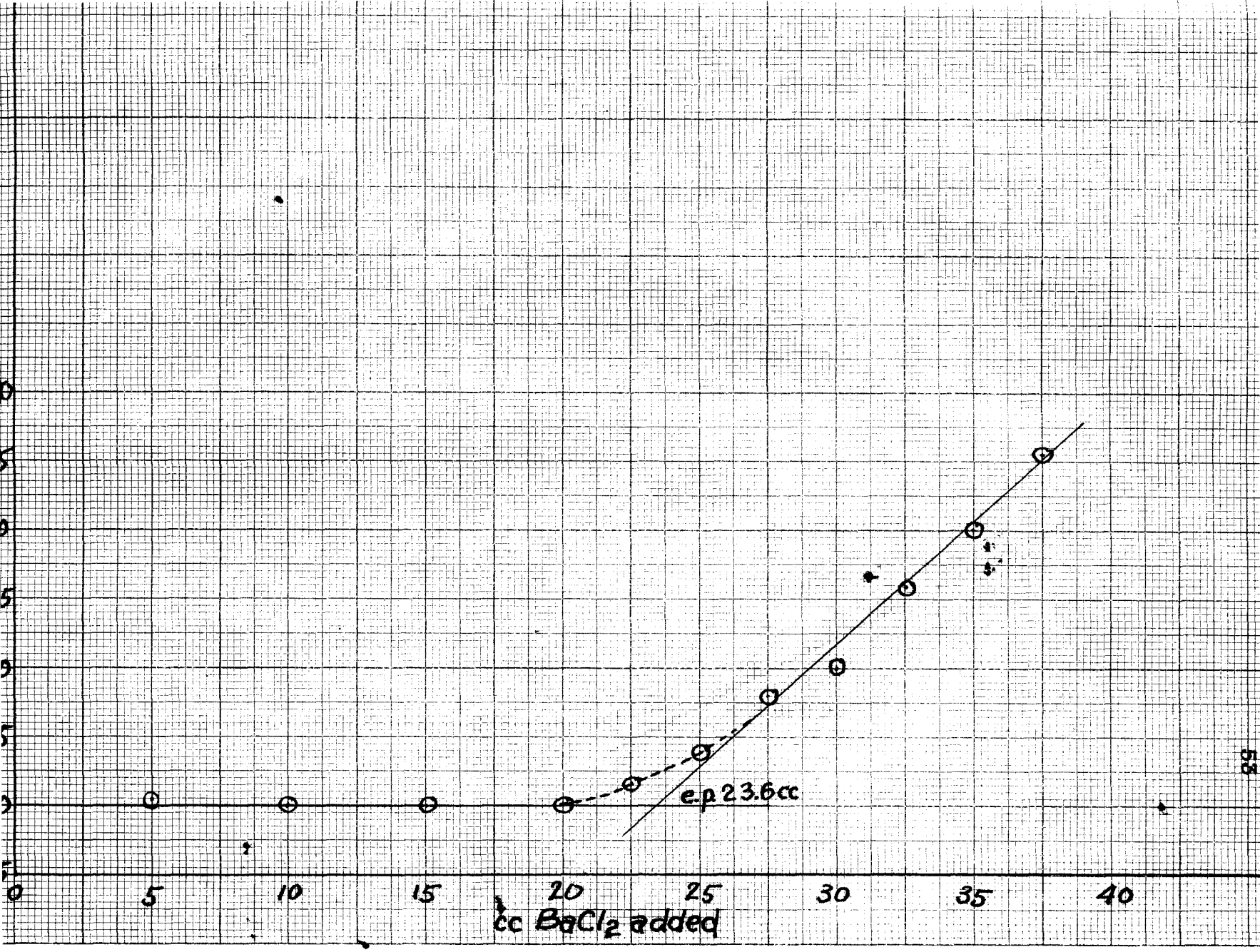
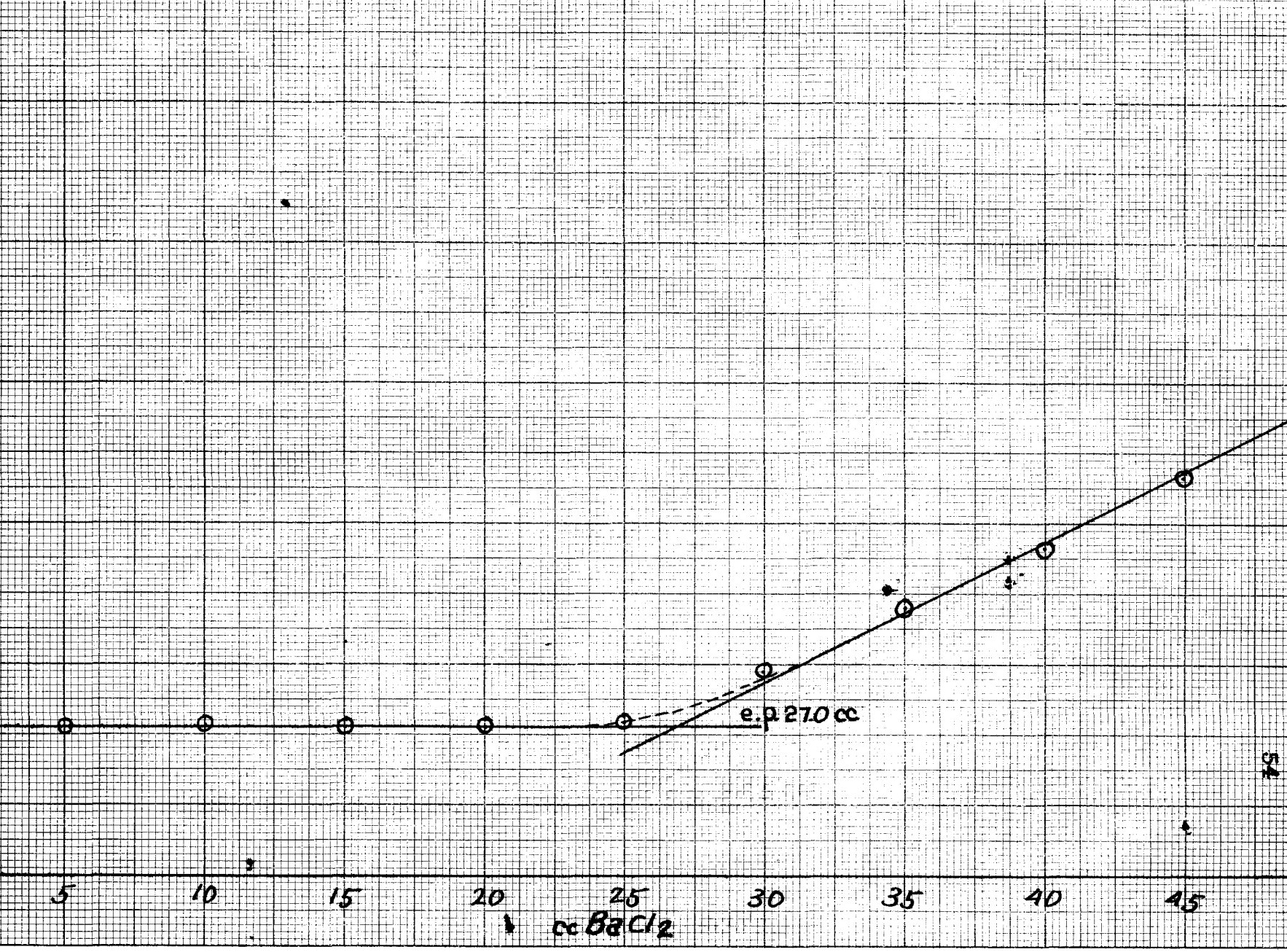

e.p 23.6cc
0
5
10
15
20
25
30
35
40
cc $BaCl_2$ added



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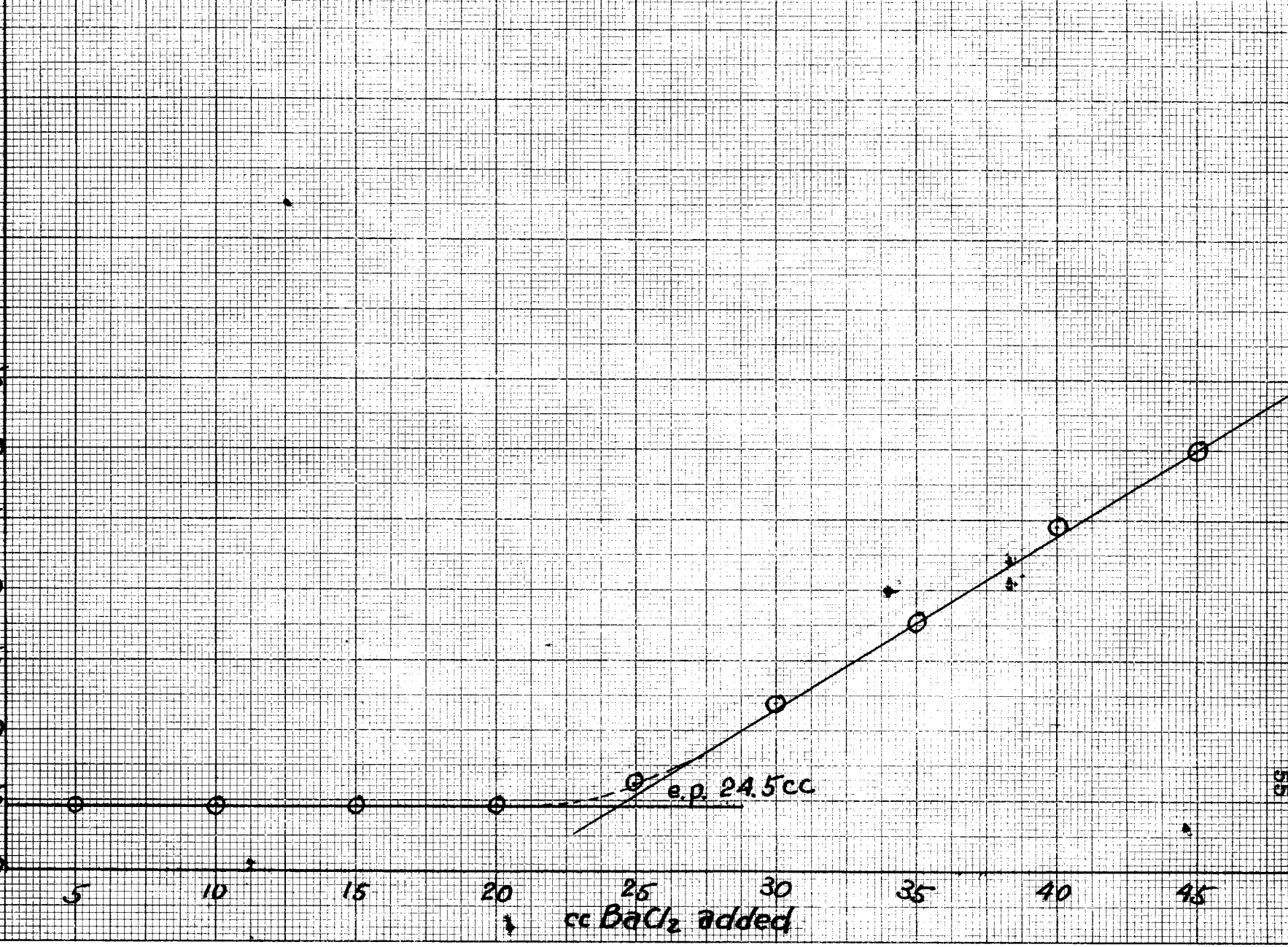

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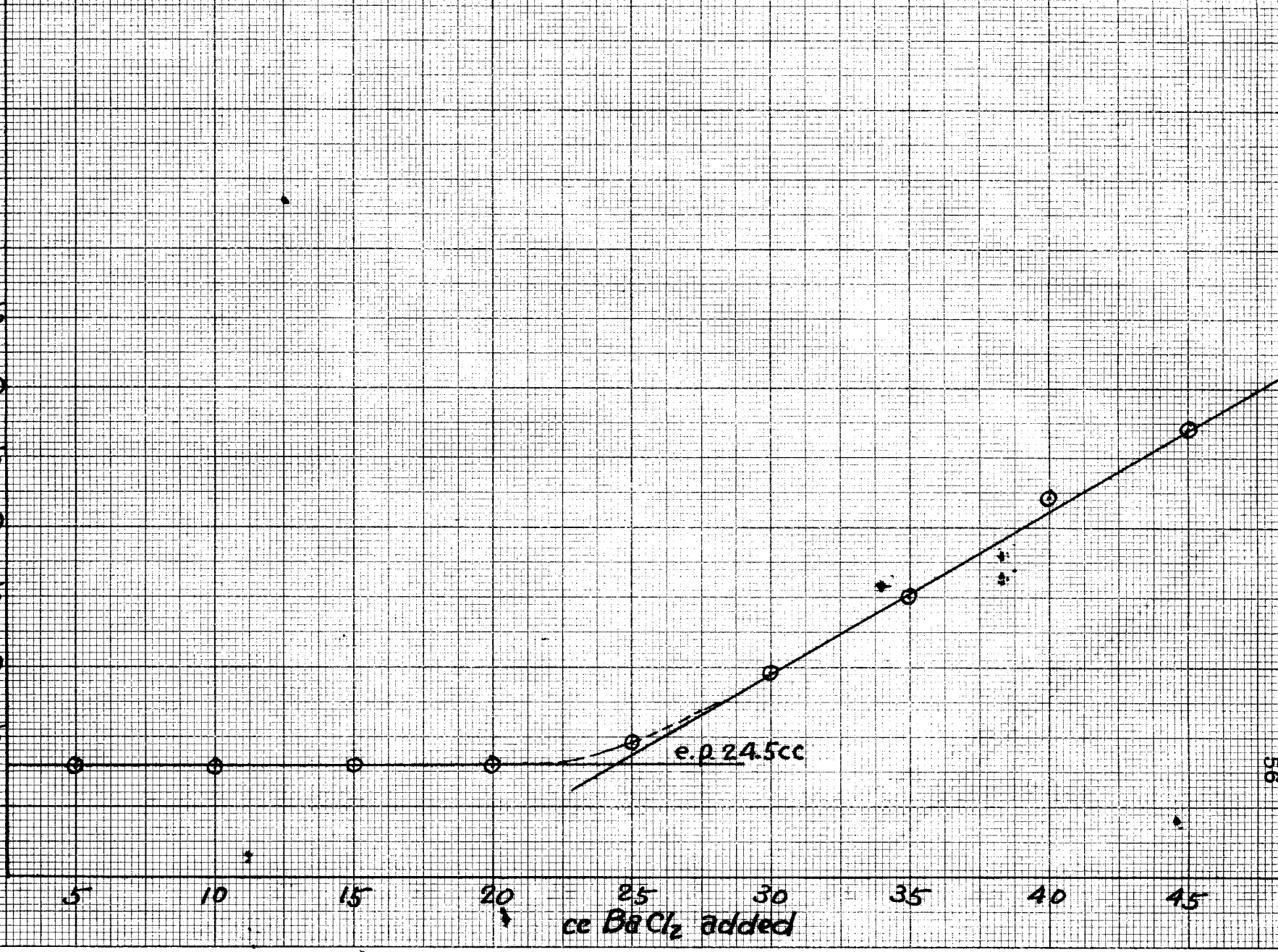
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40
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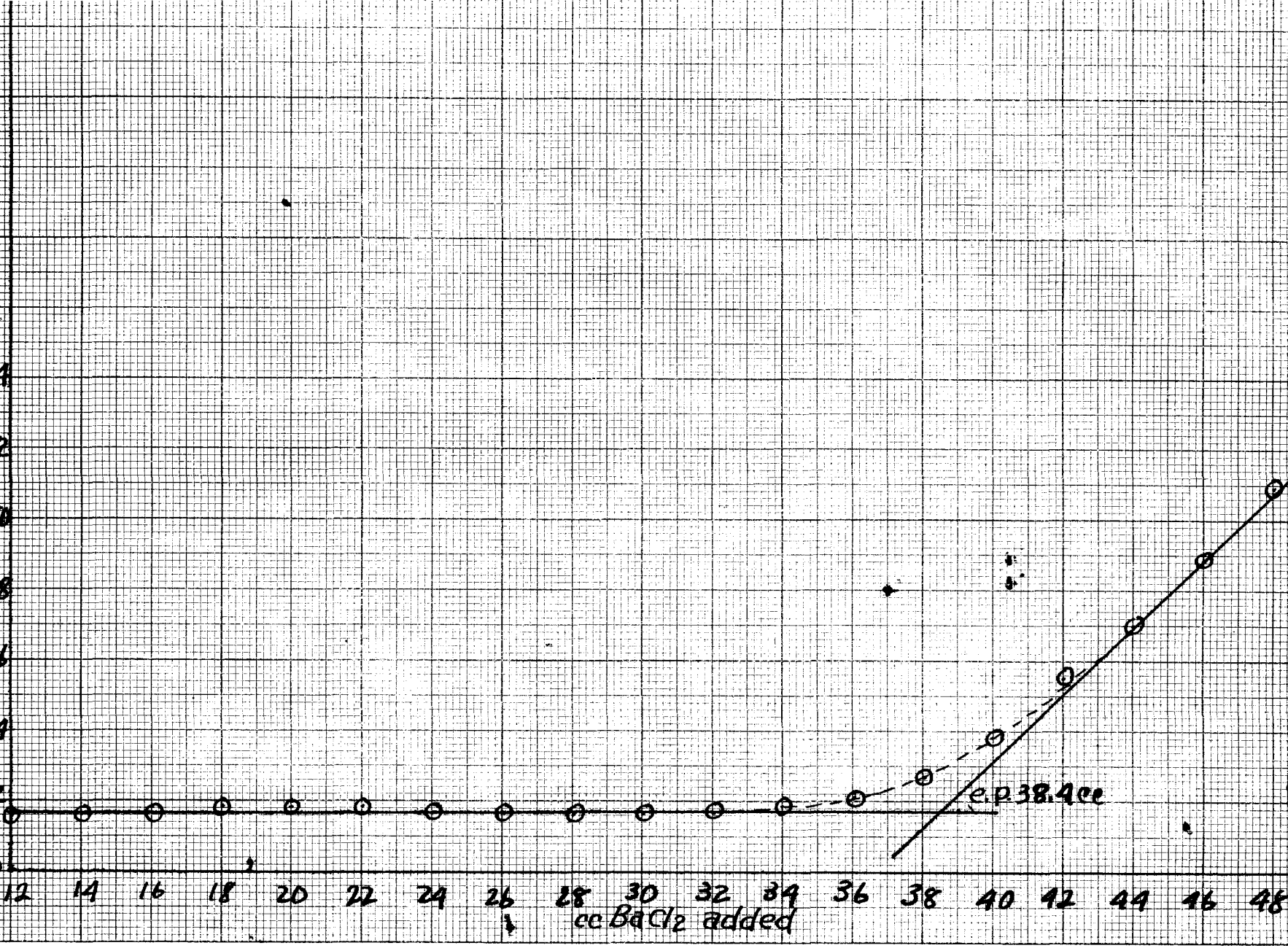
cc $BaCl_2$ added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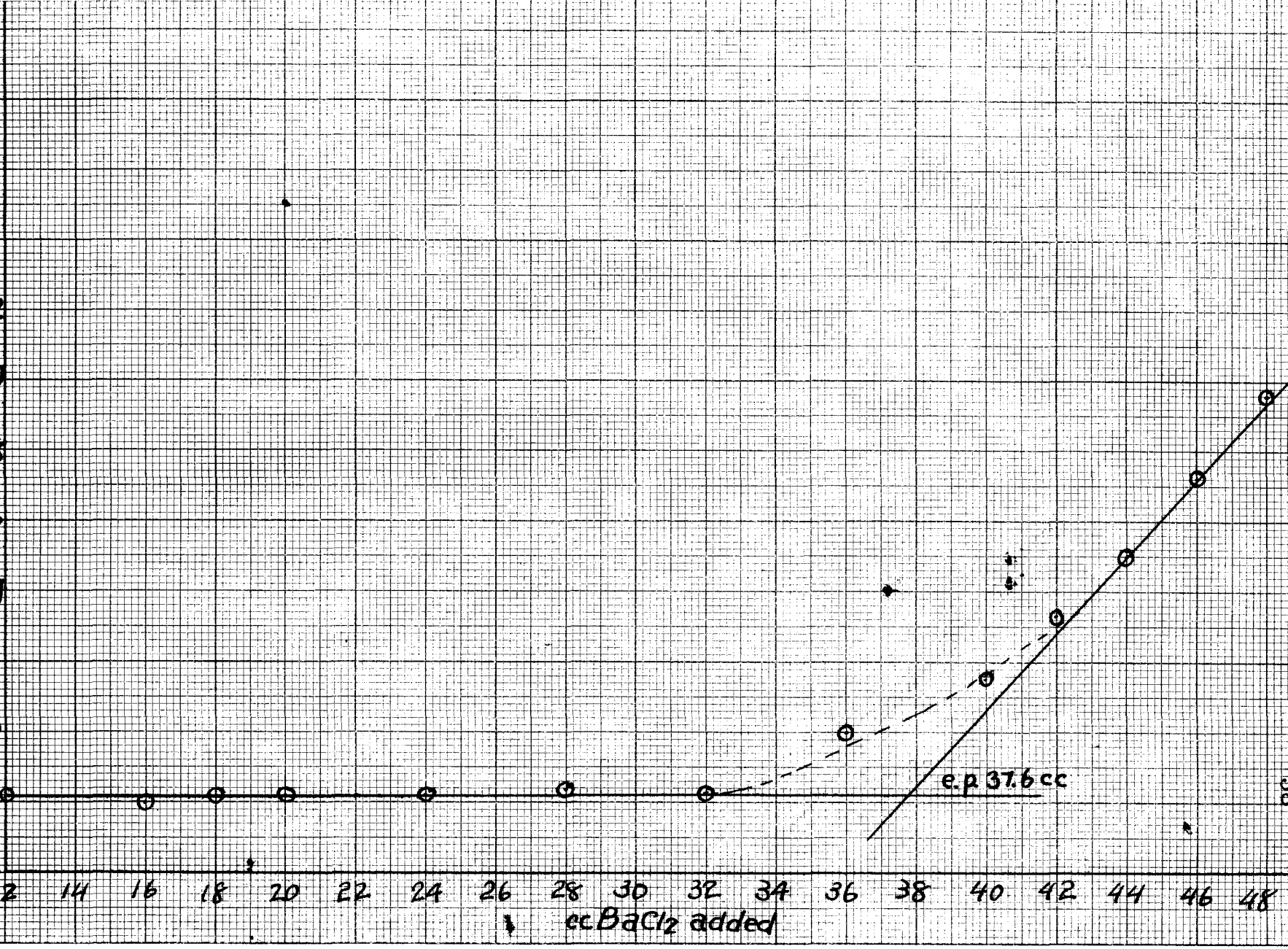
cc BaCl2 added
e.p. 38.4 cc

GRAPH 25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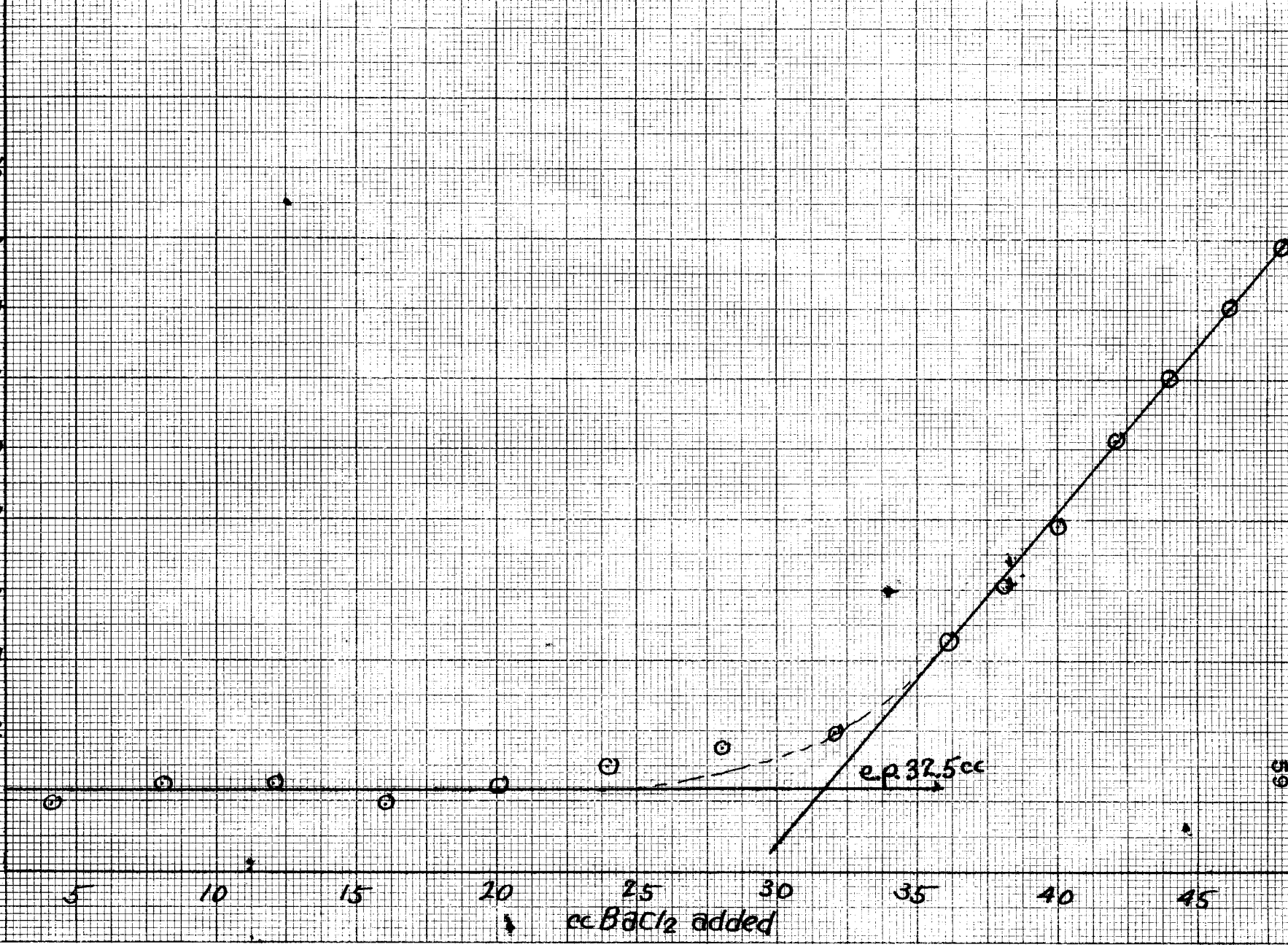
48
cc BaCl2 added

GRAPH 26



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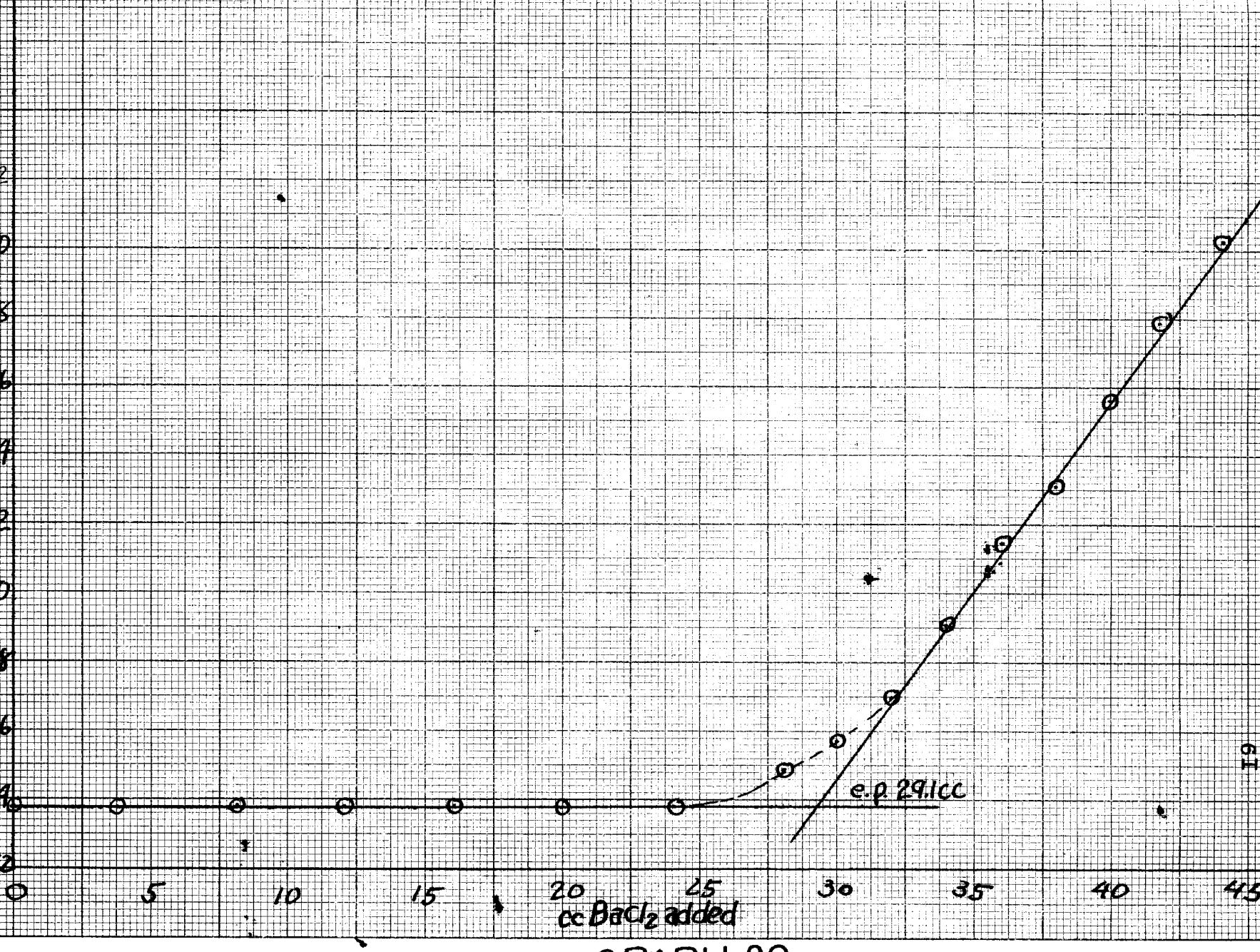
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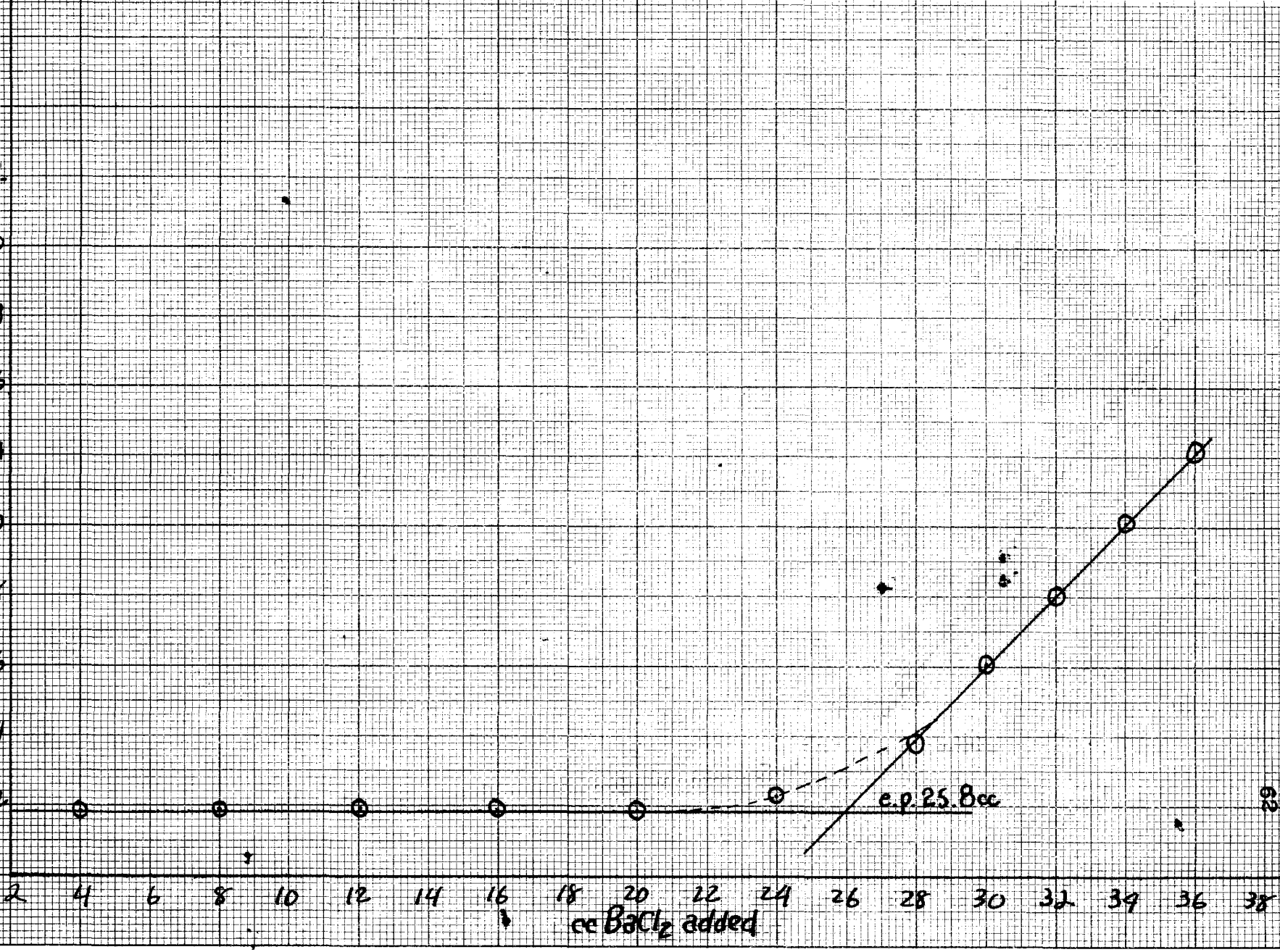
40
45
cc $BaCl_2$ added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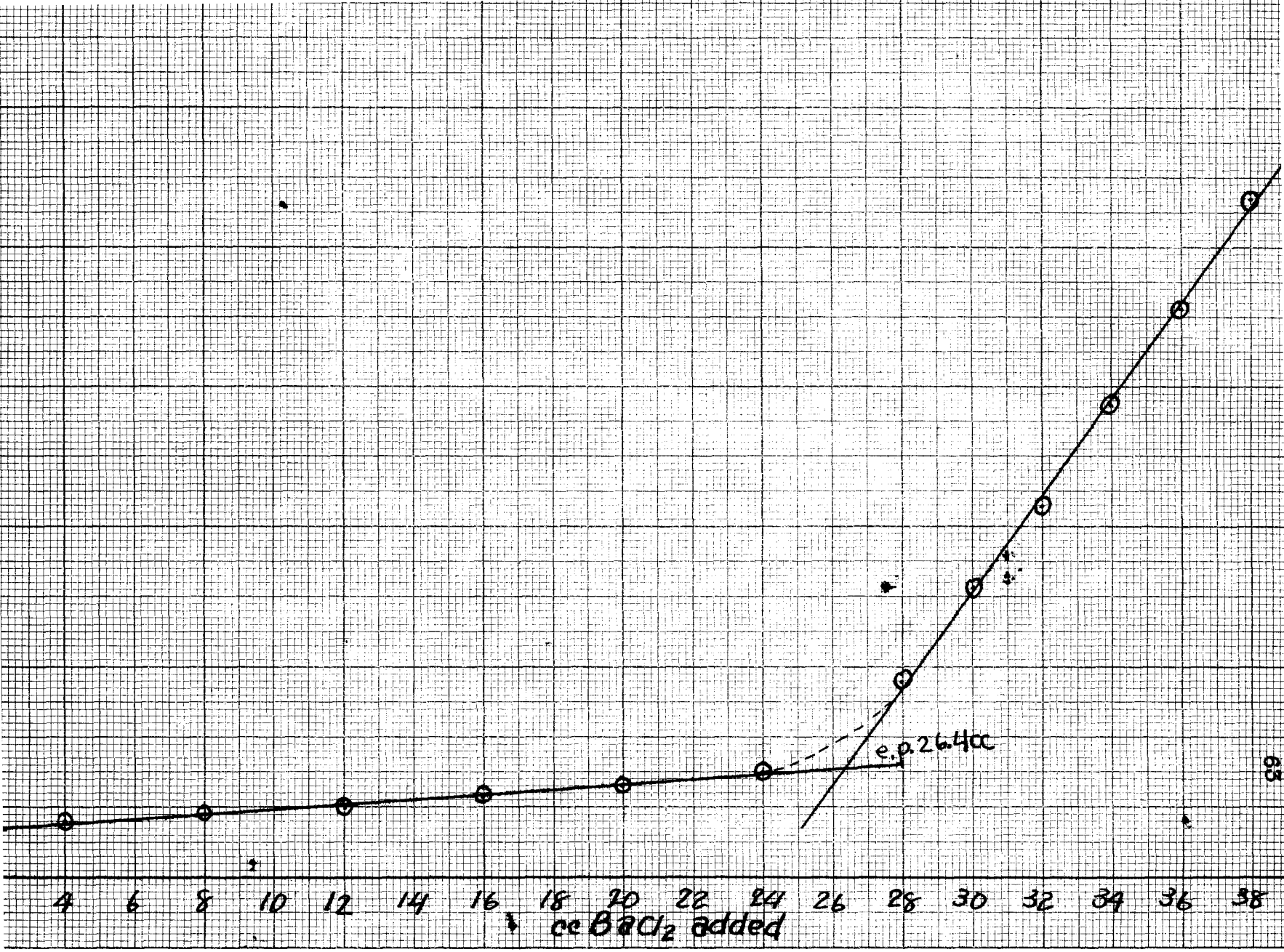
cc $BaCl_2$ added

GRAPH 20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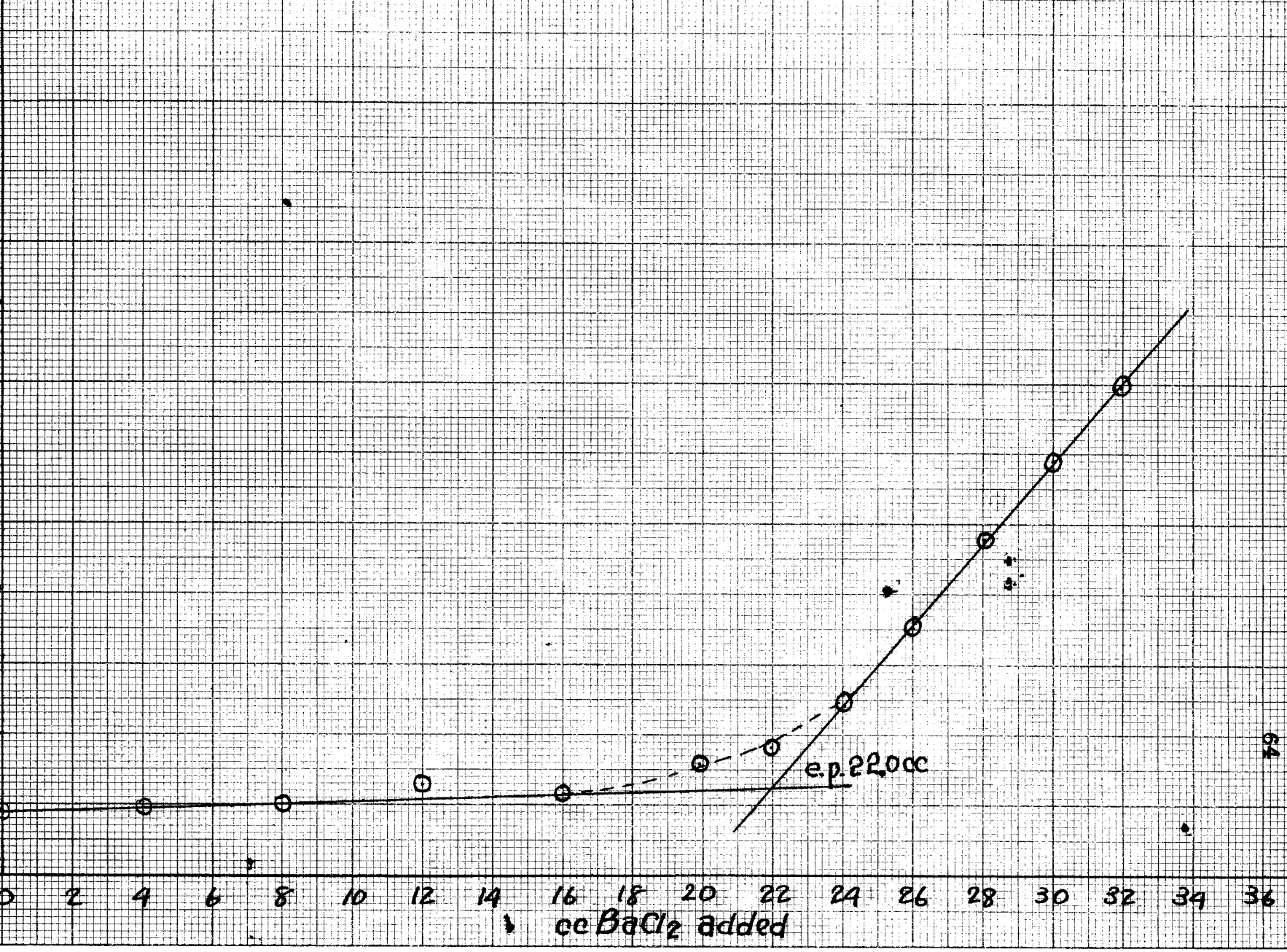
cc $BaCl_2$ added

GRAPH 21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32
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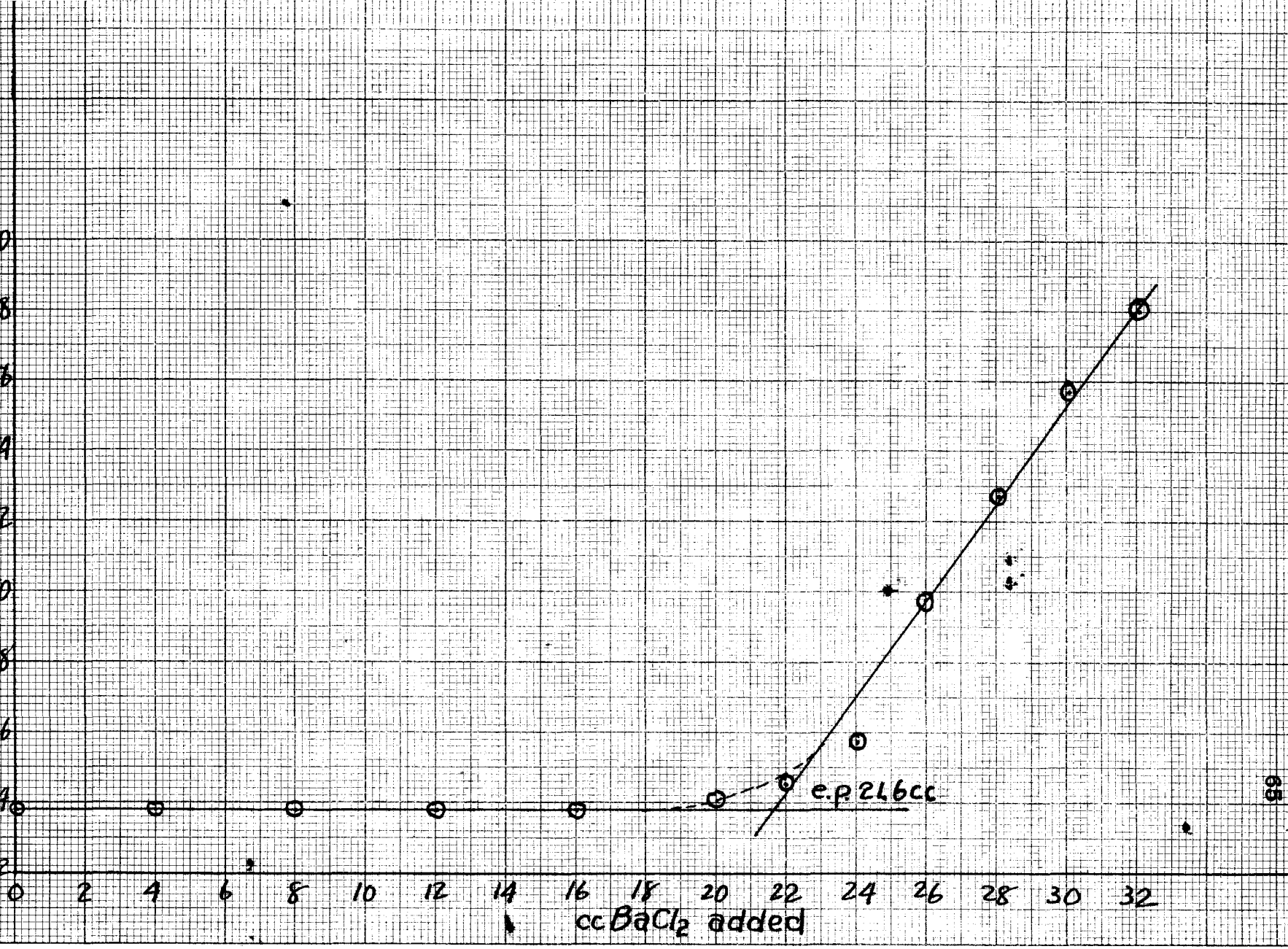
36
cc $BaCl_2$ added

GRAPH 32



GRAPH 33

X. TITRATION OF SILVER NITRATE WITH SODIUM CHLORIDE

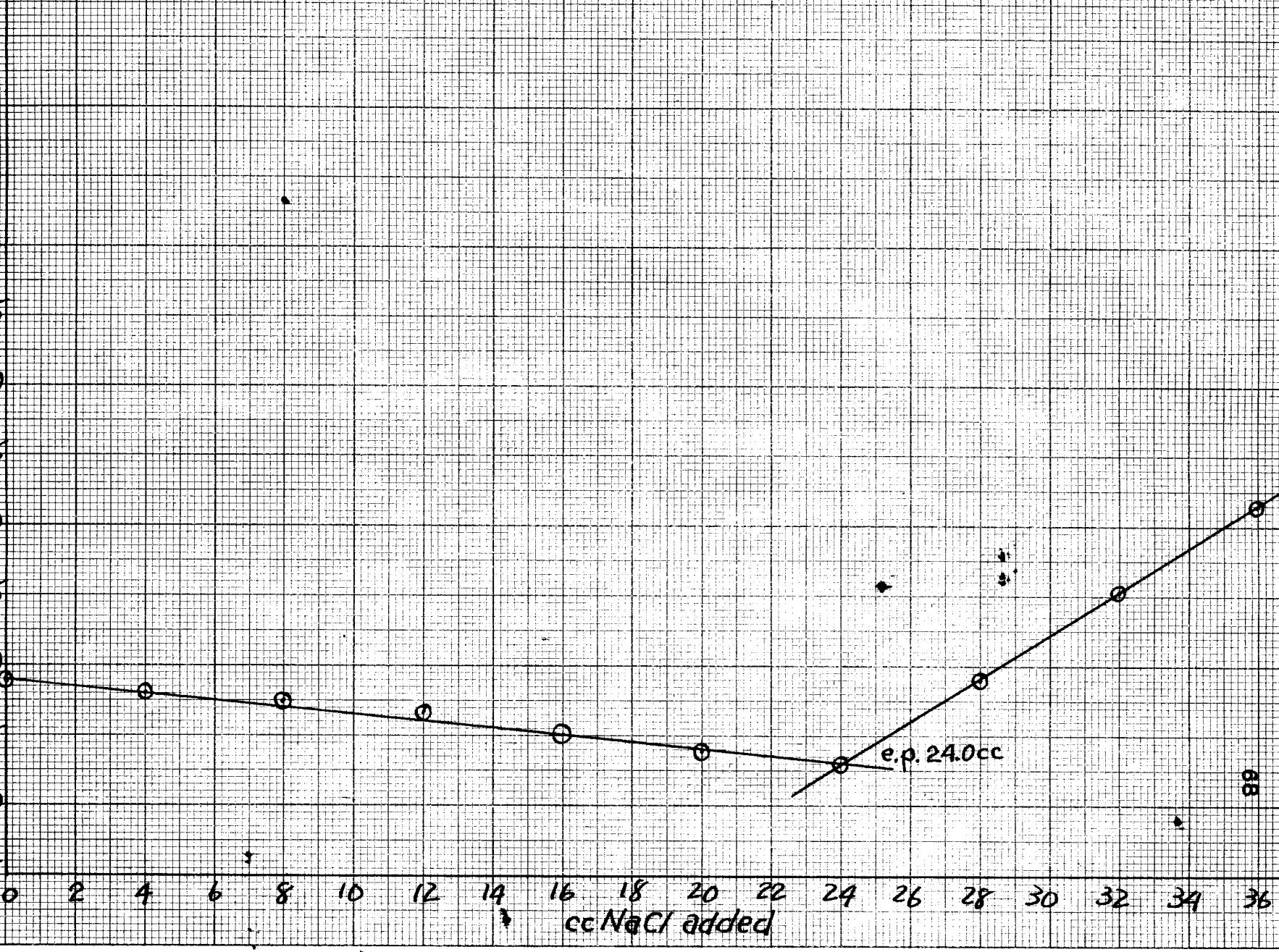
As silver ion is removed from a solution by precipitation with sodium chloride, chloride ion remplaces silver ion and since the mobility of the sodium ion is less that that of the silver ion, conductance decreases. Table 7 shows results from data on three such titrations. The average deviation from the mean is .4% and the error is 2.4%

TABLE 7

Graph No.	34	35	36
cc. $AgNO_3$(.I080-N)	20.0	20.0	20.0
cc. NaCl (.0874-N)	Conductivity		
0.0	49.5	47.6	47.6
4.0	48.0		
5.0		46.3	46.I
8.0	47.4		
I0.0		45.0	45.0
I2.0	46.7		
I5.0		43.8	43.8
I6.0	45.0		
20.0	43.8	42.7	42.5
24.0	43.I		
25.0		42.7	42.2
28.0	49.0		
30.0		5I.0	50.5

TABLE 7 (continued)

	34	35	36
32.0	55.3		
35.0		58.5	57.8
36.0	6I.4		
40.0		66.2	65.8
45.0		75.2	73.0
50.0		82.0	8I.3
end point	24.0	242.	24.2
e.p. calc.	24.7	24.7	24.7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2
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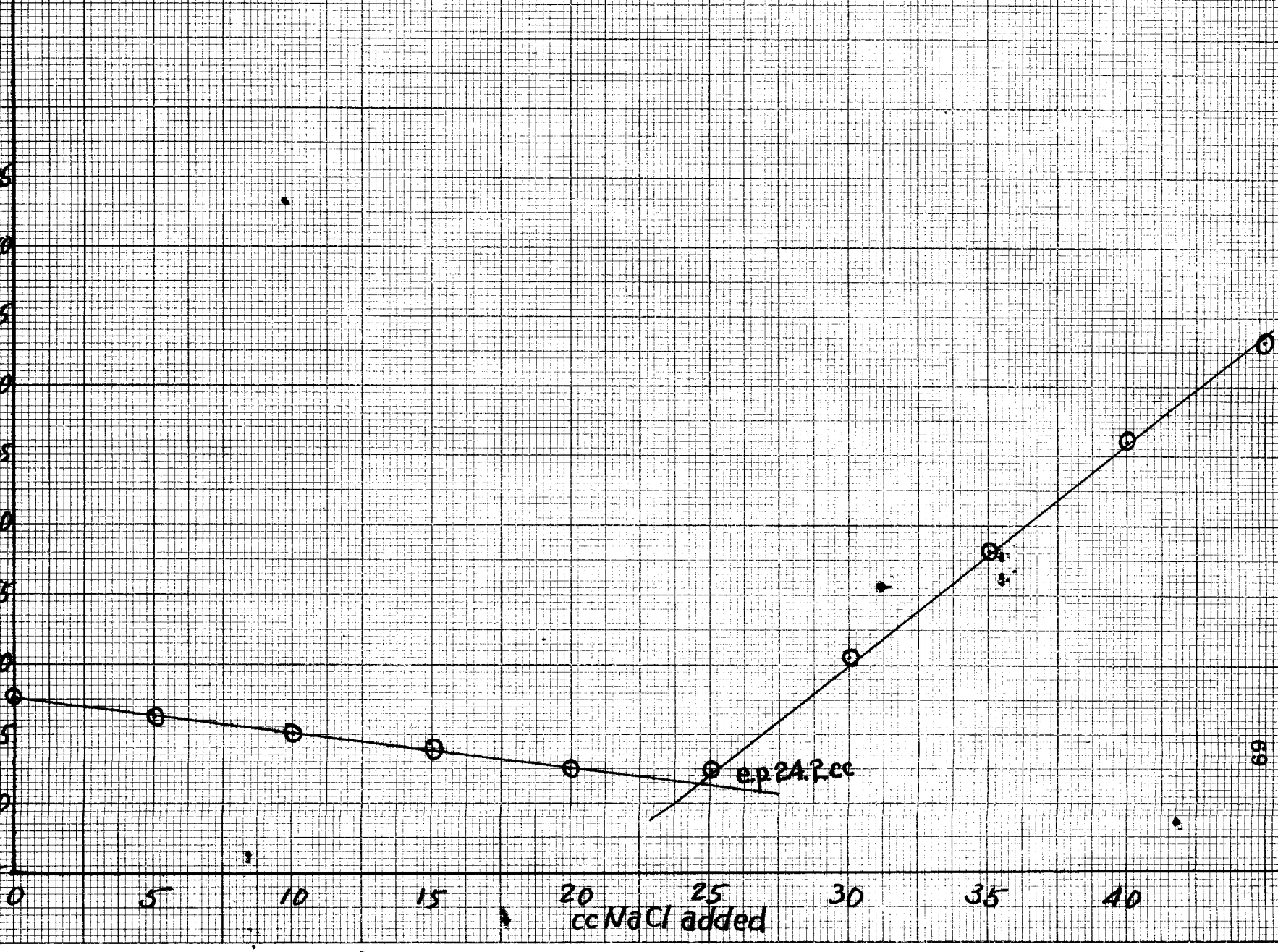
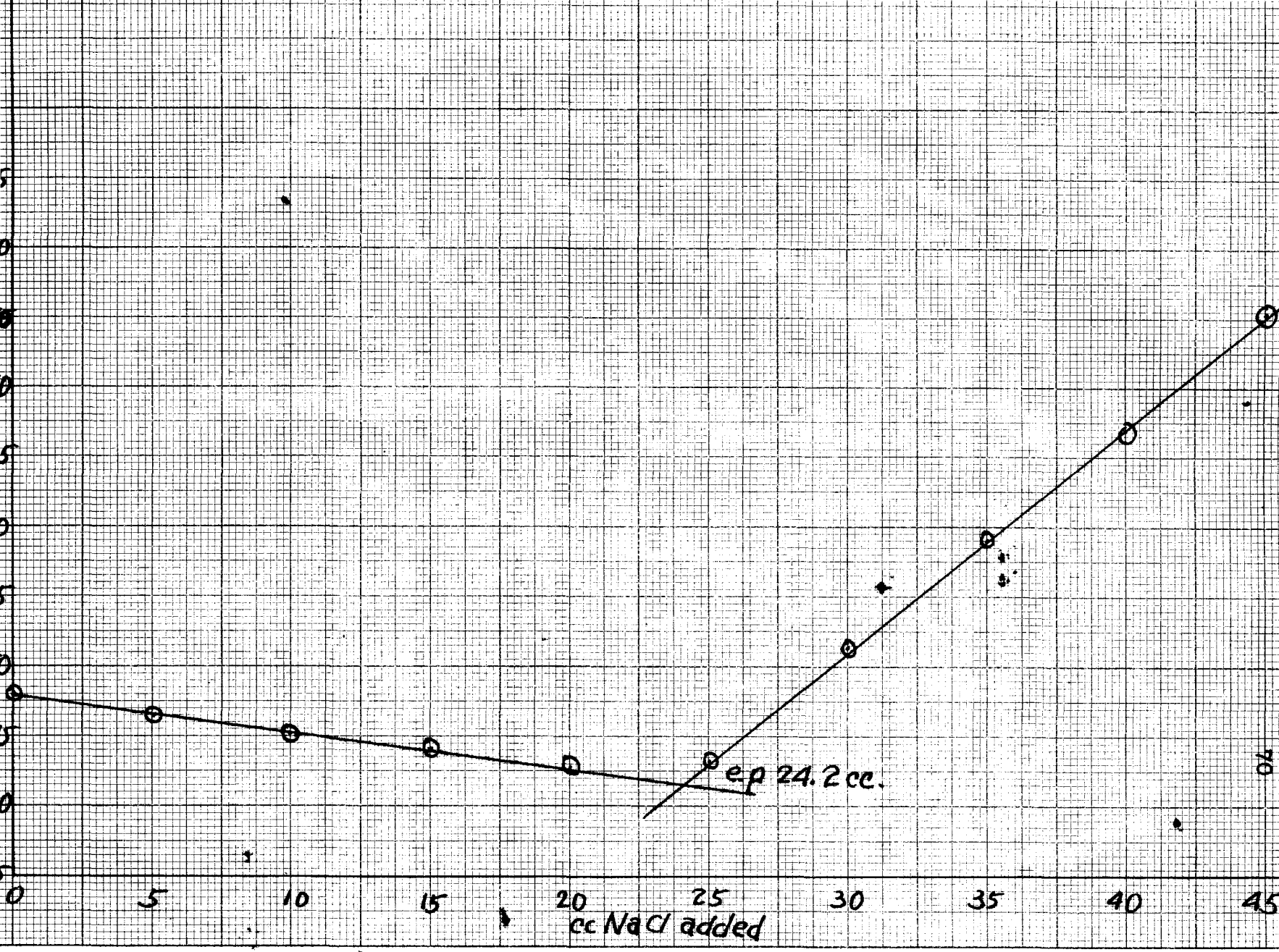
32
34
36
cc NaCl added

GRAPH 24



GRAPH 25



GRAPH 20

XI. CONCLUSIONS

1. Since the dynamometer is very accurate and precise for some types of titrations, we may conclude that it is an a adequate instrument for conductometric titrations. The inaccuracy in certain titrations is not due to the instrument but rather to variables which have not been detected and corrected for by appropriate technique.

2. The dynamometer has possibilities of being usedin certain types of titrations where indicator methods are exceedingly difficult and, as in the case of a weak acid - weak base, where even potentiometeric methods fail. Furthermore, turbid solutions offer no difficulty.

3. The simplicity whith which a conductometric titration may be run with the differential dynamometer make it a valuable aid in such analyses.

4. Because the indicator needle reads continuous values, slight changes on either side of the equilibrium point can easily be noticed. With the ordinary set-up these slight variations are apt to go unnoticed, only equilibrium readings being taken. Thus a clearer insight into the mechanism of a reaction may be obtained.

5. In brief, the differential dynamometer is suitable for conductometric titrations in place of the usual Wheatstone bridge arrangement.

XII.BIBLIOGRAPHY

I. Millard, Physical Chemistry for Colleges, third edition, I93I, McGraw-Hill

2. Britton, Conductometric Analysis, I934, Van Nostrand

3. Kolthoff and Sandell, Textbook of Inorganic Quantitative Analysis, first edition, I936, Macmillan